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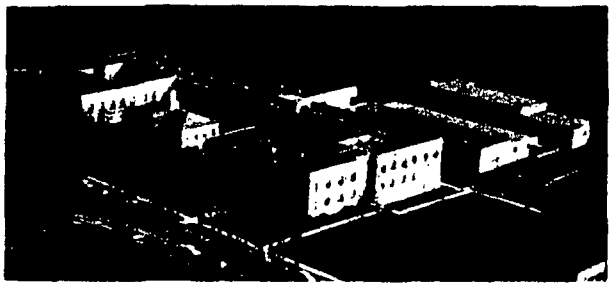

THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

Project 2419

RESEARCH ON SMELT-WATER REACTIONS

Report Seven

to

ADVISORY TECHNICAL COMMITTEE

1. Seventh Activity Report of Project Co-ordinator, IPC Project 2419
2. Progress Report of The Babcock & Wilcox Company to August 27, 1965
3. Progress Report of Combustion Engineering, Inc. to August 27, 1965

September 22, 1965

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

RESEARCH ON SMELT-WATER REACTIONS

SEVENTH ACTIVITY REPORT OF PROJECT CO-ORDINATOR

TO ADVISORY TECHNICAL COMMITTEE

Project 2419

September 22, 1965

In view of the tentative nature of research results and the intermediate stage of the research here reported, readers are cautioned against drawing premature conclusions and are advised to await definite recommendations which will be offered when the significance of the technical work has been confirmed and conclusions become warranted.

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THE INSTITUTE OF PAPER CHEMISTRY
Appleton, Wisconsin

RESEARCH ON SMELT-WATER REACTIONS
SEVENTH ACTIVITY REPORT OF PROJECT CO-ORDINATOR
TO ADVISORY TECHNICAL COMMITTEE

This report covers activities of the Project Co-ordinator from June 23 to September 22, 1965. Work by the research organizations of The Babcock & Wilcox Company and of Combustion Engineering, Inc. is presented in the attached reports, covering the period from June 4 to August 27, 1965. The Project Co-ordinator visited the B&W Research Center on August 19 and 27 and met with B&W representatives in Chicago on September 21. Discussions were held at the Kreisinger Development Laboratory of CE on September 8-10.

Studies of the chemical aspects of smelt-water reactions have been extended by Babcock & Wilcox research to contact of liquid water with molten smelt. Confirming earlier experiments with smelt and water vapor at B&W, hydrogen generation has been shown, accompanied by the production of smaller amounts of carbon monoxide and carbon dioxide. Significant proportions of the water are reacting on injection into smelt, in amounts varying from 10 to 55%.

Substantiating the work of B&W on hydrogen evolution, the generation of hydrogen from smelt-water contact has also been consistently observed, largely on a qualitative basis, in the experiments conducted by Combustion Engineering during more than the past year. When smelt at CE has been initially heated to a temperature above its explosive range, injections of water into smelt in an air atmosphere result in evaporation of water and burning of hydrogen on the smelt surface. This behavior may be repeated with several successive injections of water until the smelt cools to within the

explosive range and an explosion occurs. In these experiments, the high temperature level of molten smelt provides an ignition source and the hydrogen burns nonexplosively since the air provides sufficient oxygen to support combustion. In the absence of sufficient oxygen to support combustion, the hydrogen might form a fuel-rich gas mixture which could later explode if mixed with air in combustible proportions in the presence of an ignition source.

In considering the significance to furnace explosions of water gas generation, and subject to further work by B&W, it appears to the Project Coordinator that the above reasoning would also apply to hydrogen and carbon monoxide produced from water in contact with hot carbon in the char bed. As a third source, combustible gases can be generated from black liquor pyrolysis and probably are produced, for the most part, at temperatures below ignition levels. These gases are therefore not as likely to be burned at the point of origin, and they should be regarded as a potential hazard whenever conditions for the production and ignition of an explosive gas mixture exist. We have no indications that hydrogen or other combustible gases are generated by reactions which are explosive in themselves.

The recent B&W observation of a possible correlation between production of CO and CO_2 and the violence of smelt-water interaction may indicate an influence of chemical reaction on the energy release rate. Furthermore, present work by B&W on the possible presence of elemental sodium in smelt may indicate the need to recognize a hazardous chemical smelt-water reaction involving sodium.

The previous B&W progress report (July 1, 1965) proposed a theory of exothermic chemical reactions based on the possibility of combination of water with Na_2O, hydration of NaOH, or solubility of water in smelt. The

present progress report from Combustion Engineering describes laboratory results which indicate that physical explosive reactions of water with smelt in the presence of Na_2O or NaOH are not significantly different than the behavior of water with smelts containing equal quantities of NaCl. NaCl is not expected to react or hydrate with water and it influences the behavior of physical smelt-water explosions by increasing the intensity without changing the basic nature of the explosion. It is, therefore, concluded that Na_2O and NaOH, which act similarly to NaCl, are not major factors in the mechanism of the physical smelt-water reactions being studied at CE, although the concentration of these additives influences the intensity of the explosion.

The extreme rapidity of the physical smelt-water explosions at CE, as indicated by a pressure wave duration of 0.1 to 3 milliseconds, is considered to be insufficient time for a significant amount of water to become soluble in smelt, or to react chemically for the production of exothermic heat liberation or the generation of combustible gas. The pressure rise times of 100 to 250 milliseconds reported by the present B&W progress report for the initial pressure vessel experiments average approximately 100 times slower than those measured in CE laboratory explosions. Comparison of the pressure traces in the two reports indicates that there are fundamental differences between the experiments reported by the two laboratories. Additional data from the B&W experiments are essential before firm conclusions can be drawn regarding the mechanism of the reactions currently being studied at the B&W Research Center.

In addition to the work previously referred to, the Combusion Engineering progress report further clarifies our understanding of the concept of physical smelt-water reactions as applied both to laboratory explosions and to furnace explosions that have recently been studied. The emphasis

of the CE program is properly shifting from studies of the physical smelt-water explosion mechanism to efforts to develop means to prevent explosions of this type.

It has been suggested that sodium sulfate, normally present in smelt in small amounts, might prove to be an explosion inhibitor if present in larger quantities. The current CE report covers a range of sodium sulfate additions from 5 to 17.5% and shows that sodium sulfate is not effective in preventing physical smelt-water explosions. Interest continues in an additive which would truly inhibit the explosive behavior of smelt-water systems, but all trials to this point have failed to identify a promising smelt modifier.

Numerous CE laboratory experiments have demonstrated that high sulfidity smelts or smelts containing sodium chloride tend toward greater explosive sensitivity and violence. In order to test the effectiveness of safe quenching solutions under the most severe conditions, the CE program has worked with high sulfidity smelts with varying sodium chloride additions and a wide range of solutions of ammonium salts. It is encouraging that 40% ammonium sulfate solution, under a variety of conditions, has safely quenched smelts that would normally be violently explosive. Further work in this direction is well justified.

The research project continues to receive assistance from specialized consultants. Dr. G. C. Williams, M.I.T., has been a source of ready information on explosion technology. He has recently calculated the pressure traces that might be expected from combustible gas explosions in an operating furnace under a variety of assumed conditions. These pressure traces will be used in calculations now being made by Mr. R. R. Robinson, Illinois

Institute of Technology Research Institute, for a structural analysis of the damage pattern of the explosion at Southwest Forest Industries, Snowflake, Arizona.

The Project Co-ordinator has continued to try to establish contact with sources of information which might be helpful to this research project. It has been thought that smelt-water explosions might have some features in common with volcanic action, and inquiries to the U. S. Geological Survey led to a meeting of H. S. Gardner and W. Nelson with Dr. Edwin Roedder, experimental geologist, in Washington, D. C. While the discussion was an interesting one, we were unable to establish any meaningful relation between our work and the research with which Dr. Roedder was familiar. Contacts have recently been made, largely by telephone, with the program on Chemistry of Molten Salts of the Gordon Research Conferences, the Oak Ridge National Laboratory, the Advisory Committee on Hazardous Materials of the National Academy of Sciences-U. S. Coast Guard, the Safety and Fire Protection Committee of the Manufacturing Chemists' Association, the Safety Directors of the du Pont, Dow Chemical, and Sun Oil companies, the research departments of E. F. Houghton & Co., and American Oil Company, and Dr. George T. Austin, Washington State University. While these various contacts have touched upon a wide range of interests in molten salt and safety technology, we have found no previous experience or present research activity in the scientific fundamentals which relate to our problems in research on smelt-water reactions.

In response to a request from the Project Co-ordinator to sponsor companies of this project, general information and recorder charts from oxygen-combustible analyzers have been furnished for study of fourteen emergency situations. There is no consistent pattern relating the furnace atmospheres to any particular type of emergency. In four situations

combustible gas concentrations, measured at the boiler outlet, were indicated for periods of one to five minutes at concentrations of 3.2, +5, 9.2, and +10%. In these situations, the corresponding oxygen contents were low, and no explosion occurred. When the combustible concentration dropped suddenly, the oxygen content rose equally rapidly and an air-rich condition was quickly established. Apparently, the combination of a combustible gas composition and an effective source of ignition did not occur under any of these four circumstances of power failure, loss of I. D. fan, boiler tube failure, and boiler tube failure followed by power trip of fans and liquor pump. The other ten situations studied included four cases in which the emergency shutdown procedure had included shutting down the F. D. fan and blacking out the char bed. In these situations, the combustible content of the furnace stack gas was negligible in two cases and showed brief peaks of 0.4 and 1% in the other two cases. The oxygen content was consistently high. It would appear that the pyrolysis products of the black liquor were either negligible or had been effectively burned and that the furnaces had been in no danger at any time from combustible gas explosions. It is hoped that the sponsor companies will bring to the attention of the Project Coordinator the history of any emergency situations, hopefully survived without explosions, so that the maximum amount of information may be learned from them.

In an effort to develop data on the temperatures, gas compositions, and other salient features of furnace shutdowns, The Babcock & Wilcox Company and Combustion Engineering, Inc. have under consideration, in co-operation with mill operators, a program of plant tests. The expense of these test programs is not being met by the Smelt-Water Research Project, and they are not a formal part of the program. They represent individual efforts on

the part of the boiler companies and their customers. The first of these furnace tests, at D. M. Bare Company on July 23, is reported by B&W in its current progress report. Two observers from CE and the Project Co-ordinator were present at the test. In view of the need to prevent combustible gas explosions as well as physical smelt-water explosions during emergency shutdowns, this test program is expected to contribute importantly to a better understanding of furnace behavior under simulated emergency procedures. As further information becomes available, it will be reported.

In co-operation with Wharton Nelson of CE, the Project Co-ordinator visited the plant of Allied Paper Corporation, Jackson, Alabama, to observe the results of a furnace explosion occurring on August 14. The probability of a combustible gas explosion is regarded as unlikely, since four flame-monitored gas hearth burners and four of six liquor burners were in service and the furnace operation had been steady for over thirty minutes following a blackout. Presence of wet char in the char bed, presumably accumulated during the blackout, supports the belief that the explosion mechanism was a physical smelt-water reaction. However, the absence of any readily apparent permanent localized damage in the hearth indicates that the explosive force was not severe, as compared to the earlier localized floor damage at the Georgia-Pacific Crossett mill or at Longview Fibre Company. The upper furnace wall, buckstay, and economizer roof damage was relatively light, and the furnace was restored to service in three days. The mill management was most co-operative in providing assistance for a thorough investigation of this incident.

In the course of this research, the Project Co-ordinator has observed the circumstances of nine recovery furnace explosions, with damage patterns covering a wide range of severity, requiring from three days tc ten

weeks for repairs. In six of the nine explosions, the evidence points toward the probability of a physical smelt-water explosion mechanism. These six explosions are those at Thurso, Potlatch, Fibreboard, S. D. Warren at Muskegon (secondary explosion), Georgia-Pacific at Crossett (the two later explosions which followed an auxiliary fuel explosion), and Allied Paper (August, 1965). In considering the three other explosions, the Project Co-ordinator has been unable to make a satisfactory distinction between the possibilities of a physical smelt-water explosion or a combustible gas explosion from the pyrolysis of black liquor or from chemical reactions of the char-smelt-water system. These three unresolved explosions were at Bowaters (Catawba), Allied Paper (January, 1965), and Southwest Forest Industries at Snowflake. Without attempting to present the differing viewpoints, it should be indicated that Mr. Wharton Nelson, Combustion Engineering, who visited the Allied mill with the Project Co-ordinator after the January explosion, has concluded in the present CE progress report that this was probably a physical smelt-water explosion. Similarly, representatives of The Babcock & Wilcox Company, and others, have concluded that the explosions at Catawba and Snowflake were probably caused by combustible gases generated during emergency shutdowns.

In view of these contrasting evaluations of the evidence, it is obvious that it is frequently difficult to determine with reasonable confidence the mechanism by which a recovery furnace explosion has occurred. When a physical smelt-water explosion is of sufficient magnitude to produce highly localized deformation, such evidence can be regarded as positive identification. However, physical explosions involving smaller quantities of water or of smelt, whichever is controlling, can be of such smaller magnitude that their energy is absorbed without producing localized damage. Floor tube leaks, when small, are illustrations of this type of nondestructive explosion,

giving evidence of the presence of water within the furnace by a sudden noise, positive pressure, a jar that may only open poorly-latched doors, and possibly a disturbance of the shape of the char bed. Unless a physical explosion is severe, a localized damage pattern may not be evident on subsequent inspection.

Damage from a severe physical smelt-water explosion, however, cannot be expected to be limited to the hearth of the furnace, and may not even be concentrated in the lower portion of the furnace. Damage will occur wherever the applied stresses of the decaying pressure wave from the explosion exceed the structural strength of the furnace. Since the construction is significantly stronger near the bottom of the furnace, the hearth can withstand greater stresses than can the center points of the furnace wall panels. The upper part of a recovery furnace can be expected to sustain a degree of damage corresponding to the magnitude of the pressure wave that reaches it. At the present time, we cannot distinguish, in upper furnace damage, between the effects of a combustible gas explosion and a physical smelt-water explosion, since each may produce the same generalized damage pattern at a significant distance from the point of origin of the explosion.

The current CE progress report presents a section on Theory on Distribution of Furnace Damage which calls attention to the deformation pattern observed in large I-beams supporting furnace floors in two explosions considered to have been physical smelt-water explosions. In one of these, at Georgia-Pacific (Crossett), the unsymmetrical deformation of the floor beams is well correlated with the floor tube localized depressions and is further evidence of the intense localized energy release of physical smelt-water explosions. This is the only situation in which an effort has been made to obtain a detailed pattern of localized floor beam deflections. As

a result of CE's recognition of their significance, such measurements may prove to be a useful tool in studying the effects of furnace explosions. We now intend to investigate the pattern of floor beam deflections in other furnaces which have had explosions. We hope that such measurements may help to identify the explosion mechanism.

The following general conclusions are indicated:

1. The reality of noncombustible smelt-water explosions, both in furnace explosions and in laboratory studies at Combustion Engineering, Inc., has been conclusively demonstrated.

2. The concept of physical smelt-water explosions initiated by the encapsulation of liquid water within smelt is a useful working hypothesis to explain the observed facts related to noncombustible smelt-water explosions.

3. Furnace protection from noncombustible smelt-water explosions requires prevention of the contact of smelt by any possible source of liquid water, other than strong black liquor.

4. Elimination of noncombustible smelt-water explosions requires the development of new techniques, probably additives to smelt, boiler water, or both, to prevent the physical explosive reaction of water and smelt. The present prospects for a successful development of this kind are not promising.

5. A significant improvement in the safety of emergency shutdowns after smelt-water emergencies have been recognized may result from the development of a safe quenching solution such as ammonium sulfate, or the use of strong black liquor, to rapidly cool smelt below the critically explosive temperature range in which physical explosions with water have been shown to occur.

6. The significance of smelt-water-char chemical reactions to recovery furnace explosions, other than explosions from the ignition of combustible gaseous mixtures with oxygen, remains to be demonstrated.

7. Regardless of the ultimate significance of combustible gas generation by chemical reaction or black liquor pyrolysis, air dilution to maintain a fuel-lean furnace atmosphere below the explosive composition range and/or steam inerting offer furnace protection against combustible gas explosions during emergency shutdowns.

THE INSTITUTE OF PAPER CHEMISTRY

Howard S. Gardner

Howard S. Gardner
Co-ordinator, Smelt-Water Research Project
Senior Research Associate
Administrative Staff

PROGRESS REPORT NO. 6

FOR THE PERIOD OF JUNE 4, 1965 TO AUGUST 27, 1965

TO

H. S. GARDNER, PROJECT COORDINATOR,
THE INSTITUTE OF PAPER CHEMISTRY

INVESTIGATION OF SMELT-WATER REACTIONS

Submitted by:

THE BABCOCK & WILCOX COMPANY
RESEARCH CENTER
ALLIANCE, OHIO

September 15, 1965

PROGRESS REPORT NO. 6 OF THE BABCOCK & WILCOX COMPANY
ACTIVITIES ON INVESTIGATION OF SMELT-WATER REACTIONS

INTRODUCTION

This report summarizes the work accomplished between June 4, 1965 and August 27, 1965 and the present status of this project. As outlined in our previous reports, our over-all objective is to determine (a) whether, and (b) which, chemical reactions occur between the smelt-char-combustion gas system with water that result in explosions. A further objective is to determine the thermal decomposition products of black liquor. Having reached an understanding of the chemical reactions taking place, a sounder basis for preventive measures and procedures may be formulated.

In our previous progress report, we showed that the reaction of water vapor with liquid smelt was largely one of hydrogen production, with the generation of smaller quantities of CO and CO_2. As the experiments were carried out under steady-state conditions (approximating equilibrium) the yields of gases would be expected to be greater than would be obtained from a fast liquid water-smelt reaction. Therefore, our experimental laboratory work was concentrated on this latter reaction during this report period. In addition, as a result of our work on the study of the products of black liquor decomposition reported in Progress Report No. 4, a shut-down procedure test was carried out at the D. M. Bare Co., Roaring Springs, Pennsylvania.

SUMMARY OF WORK

1. The molten smelt-liquid water reaction has been studied experimentally with the following tentative results:
   (a) Hydrogen yields ranged from 11%-55%, depending upon experimental conditions. Any of these amounts would be

explosive if mixed with air in combustible proportions and an ignition source were present.

(b) High smelt temperatures favor higher yields of hydrogen.

(c) Yields of hydrogen were not markedly affected by sulfidity.

(d) There is an apparent inverse relationship between hydrogen yields and CO_2 yields.

(e) One test with green liquor showed an increased yield of hydrogen.

(f) One test, 3 cc of water vs 1 cc of water, showed that the larger quantity of water reduced the hydrogen yield slightly.

(g) Each of six successive injections (except the second) of water into sodium carbonate gave lower yields of CO_2 and a final yield of 4.4% NaOH.

2. Pressure transducer measurements showed pressure rises from 3-7 psi from the smelt-water reaction. Rise times, in general, were approximately 100-250 milliseconds. Smelts that gave the sharpest rises were usually blown out of the crucible. A rough correlation could be made between CO_2 production and a low order of indicated violence.
3. A study of the water-gas reaction was initiated.
4. Test planning and equipment preparation were carried out in order to study whether sodium is soluble in smelt at operating temperatures.
5. A successful test of a shut-down procedure, based on the concept of no black liquor quenching, no primary air flow and an air-rich atmosphere in the unit at all times was carried out.

CONCLUSIONS

As a result of our work during this quarter, we have reached the following tentative conclusions:

1. Liquid water, injected into molten smelt, can react chemically and result in the production of significant quantities of hydrogen. Carbon monoxide and carbon dioxide are also formed in relatively small amounts.
2. Based upon one test, it appears that Kraft recovery boilers can be shut down safely and successfully with no gaseous explosive hazard, using the concept of insuring an air-rich mixture in the unit at all times.

THEORETICAL

Water-Gas Reaction. The water-gas reaction is the well known reaction taking place between carbon and water to yield CO and hydrogen.

$$C + H_2O \rightleftarrows CO + H_2 \qquad \Delta H = +32{,}450 \text{ Kcal}$$

This reaction is pertinent to the smelt-char-water explosion problem from at least two points of view: (a) it is a potential source of explosive gas, (b) it generates two moles of gas from every mole of water reacting, hence could contribute to a pressure rise.

This reaction, however, tends to be self-quenching, as may be inferred from its positive ΔH. Furthermore, although the equilibrium is favorable at all temperatures above 1000 F, kinetic studies (1) have shown that yields approach equilibrium at about 2000 F. Therefore, in view of these factors, this reaction is being examined theoretically in order to obtain some insight as to its possible significance. To date, no firm conclusions have been reached as to the reaction's contribution to the over-all explosion problem.

EXPERIMENTAL

Apparatus

A diagram of our experimental apparatus is shown in Figure 1. This apparatus

is basically a standard Autoclave Engineer's 1 gallon reactor, designed for 5000 psi at 650 F and modified for the present experimental purposes. A small furnace, wound with 16 gauge Kanthal heater wire was inserted into the bottom portion of the reactor. The furnace is insulated from the reactor proper with insulating brick on the bottom and Kaowool around the sides. A stainless steel crucible (2 1/4" I.D., 1 1/2" deep) fits into the furnace and is formed such that it contains a protective shoulder over the furnace and its insulation. A sheathed thermocouple indicates the melt temperature. The water injection system consists of a hypodermic syringe, adjustable to furnish a fixed amount of water. The syringe tubing, stainless steel, was .066" O.D. and .0465" I.D.. A Conax fitting was attached to the connecting sheath to form a gas-tight connection for the water injection inlet system. The static pressure generated was measured with a pressure gauge, as well as a mercury manometer. The transient pressure peaks were indicated by a Kistler 601H Quartz pressure transducer, and a Honeywell Visicorder. An inlet-outlet system allowed the vessel to be evacuated, filled with helium gas, and gas samples to be taken for analysis.

PROCEDURE

Smelt Preparation

Two different procedures for preparing synthetic smelt were followed. One procedure, designated as A, was as follows: The calculated amount of $Na_2S \cdot 5H_2O$, reagent grade and Na_2CO_3, reagent grade to give a 35% NaS-65% Na_2CO_3 smelt was heated in a graphite crucible in a muffle furnace to 2000 F and held at that temperature for 10 minutes. The crucible was cooled to room temperature in an inert atmosphere, the smelt removed and stored in a desiccator prior to charging into the reaction apparatus. Procedure B followed the procedure outlined in previous reports; i.e., reagent grade $Na_2S \cdot 9H_2O$ was dehydrated by

heating to 500 F under a vacuum, then mixed in the proper amount with Na_2CO_3, and this dry mixture charged to the reactor.

Test Procedure

The sample charge (115-125 gms) was placed in the crucible in the reactor and the reactor was then evacuated and the air atmosphere replaced with helium at one atmosphere pressure. The crucible furnace was then turned on and the charge heated to 1800 F for ten minutes, then the temperature allowed to cool to test temperature. The gas was analyzed, then drawn off and replaced with helium at one atmosphere pressure. The thermocouple leads were attached to the recorder. The Visicorder was actuated (generally at 1 in./sec) and distilled, deaerated, room temperature water was injected through the hypodermic tubing. The pressure rise was noted on the manometer and a gas sample, drawn through a dehydrating agent, was taken and analyzed on the gas chromatograph for CO_2, CO, and H_2. If no fast peak was observed on the Visicorder, the gas atmosphere was again replaced with one atmosphere of helium and the injection procedure repeated. In most cases where sharp pressure peaks were observed, it was found that the smelt had been blown out of the crucible and most was found symmetrically distributed around the shoulder of the crucible, with some splattering on the sides of the vessel.

RESULTS

A total of ten runs were made, two of which were made on pure sodium carbonate, the remainder on synthetic smelts. A summary of these results is shown in Table I.

The smelt charge in Run B-2 was most unusual in that it apparently contained a large residual quantity of sodium hydroxide.* This smelt also contained a significant amount of carbon from the graphite crucible.

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*Conventional chemical analysis does not distinguish between sodium hydroxide and sodium oxide. In this and future references to sodium hydroxide, it should be kept in mind that the sodium hydroxide could possibly be sodium oxide, or a combination of sodium hydroxide and oxide.

In the analysis of the results, this run has therefore been disregarded.

DISCUSSION AND SIGNIFICANCE OF RESULTS

Hydrogen Yields

It will be noted from Table I that all injections of water into smelt yielded significant amounts of hydrogen, although the amounts found were somewhat dependent upon the experimental conditions. Thus, it appears that an item of particular significance to the Kraft recovery explosion problem is that hydrogen is perhaps generated in sufficient quantities to result in a gas explosion if suddenly mixed with air in combustible proportions and an ignition source is present. It should be kept in mind that, in our viewpoint, there are several interrelated variables affecting the yields of the various gases, and that to draw firm conclusions would require a large number of carefully controlled experiments. Nevertheless, there are some effects that are indicated by our results and are discussed below.

Effect of Temperature

The effect of temperature on hydrogen yields can be most clearly indicated by a consideration of runs B-3, B-4, B-6, and B-7 in which the smelt was prepared by the same procedure and investigated at a range of temperatures.

Figure 2 shows the trend toward increasing hydrogen yields at higher temperatures.

This increased yield of hydrogen is consistent with equilibrium constant calculations of the effect of temperature on the reaction

$$1/4\ Na_2S + H_2O \rightleftarrows 1/4\ Na_2SO_4 + H_2$$

and verifies that in this temperature range the reaction of water with sodium sulfide is endothermic. It furthermore is consistent with the viewpoint that the experimental explosion studies carried out by B&W some years ago could be explained by the production of hydrogen and subsequent ignition. The explosions

obtained in that study became more pronounced at higher temperatures and this would be expected if the hydrogen production increased as a function of temperature.

This increased hydrogen production at higher temperatures, on the other hand, is inconsistent with our theoretical equilibrium calculations of a smelt-water system shown in our last progress report. These calculations indicated that the higher temperature should favor CO_2 and CO production from the reaction

$$Na_2CO_3 + H_2O \rightleftarrows 2NaOH + CO_2$$

and

$$4CO_2 + Na_2S \rightleftarrows Na_2SO_4 + 4CO$$

The failure to observe significantly higher yields of CO_2 at the higher temperatures implies that the kinetics of the H_2O-Na_2S reaction are favored over the H_2O-Na_2CO_3 reaction at the higher temperatures.

Effect of Sulfide

The effect of sulfide concentration on hydrogen yields is shown graphically in Figure 3. It will be noted that there is little if any correlation. While it would be expected that higher sulfide concentrations would show increased hydrogen yields, theory predicts that the dependence is relatively insensitive to sulfide concentration compared to sulfate or hydroxide.

Effect of Sulfate

It was found in previous work (Progress Report No. 5) that sodium sulfate, under steady-state conditions, approximating equilibrium, reduced the yield of hydrogen from the smelt-water (vapor) reaction. While the smelt compositions investigated during this present period contained a variable, residual amount of sulfate (.05-0.5%), no correlation could be made between the hydrogen yields and sulfate concentration. It is possible that, in these experiments, the effect

of other variables, notably hydroxide, overshadowed the effect of small differences in sulfate content.

Correlation of Hydrogen Yield With CO and CO_2

It was noted that lower hydrogen yields tended to be associated with higher values of the combined yields of CO_2 and CO. A correlation plot of the data showing this relationship is shown in Figure 4.

Effect of Hydroxide

It has been pointed out in our previous progress report (Progress Report No. 5) that the hydroxide content of smelt is a variable affecting the products of its reaction with water. Furthermore, from a theoretical point of view, if there is only a small amount, or no hydroxide present, there is a stronger tendency for the

$$Na_2CO_3 + H_2O \rightleftarrows 2NaOH + CO_2$$

reaction to take place. Thus, low initial hydroxide contents should favor higher yields of CO_2 and lower yields of hydrogen. It seemed significant that Runs B-7 and B-8, and to some extent B-10 contained the lowest hydroxide at the end of the run, and at the same time produced the largest quantity of CO_2, at least for the first two 1 cc portions added.

Thus a possible mechanism, which has been previously proposed in Progress Report No. 5, of so-called smelt sensitization appears to be the process of forming enough sodium hydroxide in the smelt so that any subsequent, possibly exothermic reaction can take place.

Effect of Green Liquor

One test of the effect of green liquor injection was made during Run B-5. As three injections of water had not produced an explosion, a further injection consisting of a 10% solution of synthetic green liquor was made. Such an

injection produced a significant pressure peak and, at the same time resulted in an increased production of hydrogen over the previous injection of water. It will be noted that there was no significantly increased yield over the first injection with water. However, because hydrogen yields tend to diminish with multiple injections, it is concluded that the green liquor injection probably gave an increased yield of hydrogen.

It will also be noted that the residue from this run contained 3.4% hydroxide, a relatively high concentration.

Effect of 3 cc vs 1 cc of H_2O

One test was carried out to check the relative yields of gas (H_2, CO, CO_2) from an injection of 3 cc of water as contrasted to 1 cc. Test B-10 shows that a somewhat lower yield of combustible gas was obtained.

Effect of Injection on Top of Smelt

In Run B-10 the water was injected with the end of the injector approximately 1" from the top of the smelt. No significant difference was noted in the gas yields.

Sodium Carbonate Runs (B-1, B-9)

There has been much speculation that the sodium carbonate-water reaction is one of purely physical generation of steam. However, there is the possibility that the endothermic reaction

$$Na_2CO_3 + H_2O \rightleftharpoons 2NaOH + CO_2$$

takes place and modifies the rate of generation of steam. Furthermore, it would be predicted that a purely physical reaction would ultimately be obtained from multiple injections of water into molten sodium carbonate until sufficient sodium hydroxide had formed so that no chemical reaction takes place (assuming that there is no exothermic hydration of NaOH). Therefore, it was pertinent

to determine the behavior of sodium carbonate, after it had been demonstrated in Run B-1 that a significant reaction took place upon multiple injections of water. It will be noted (Fig. 5) that in Run B-9, the combined yield of CO_2 + CO was initially high, then fell off at the 6th injection to 3.9% CO_2 and 0.2% CO. At the same time, chemical analysis showed that 4.4% NaOH, or 5.1 grams of NaOH had been formed from 6 cc of water.

Both Na_2CO_3 runs showed the presence of CO and H_2 and this is interpreted as an interaction of CO_2 and H_2O with the crucible or walls of the vessel. As the CO must come from CO_2, we have added these gases together as a measure of the CO_2 evolved.

The Visicorder tracings (Figs. 6-7) after the first injection differed from the first. It seemed to us that the pressure rise after the 5th injection was one of the fastest reponses. No firm conclusions could be drawn from these pressure responses.

It will be noted that at the higher temperatures of Run B-1 there was a significantly higher yield of CO and CO_2.

Interpretation of Pressure Peaks

Initial runs (B-1 to B-6) were made with the Visicorder sensitivity set for a maximum of 90 psig full scale. The pressure peaks observed were thus quite small and as a result the sensitivity was increased to read 30 psi full scale for the last four runs. Two typical peaks are shown in Figure 8 for Run B-8, a smelt considered to be, if any, only mildly explosive. As no marked explosions were observed at the higher sensitivity, no quantitative comparison of such traces can be made. It should be kept in mind that the pressure peaks are those measured 9" above the surface of the melt and would be expected to follow an inverse law, thus register much less than would be

found, say, 1" from the explosion. Consideration is being given to a further refinement of the transient pressure measuring device.

Qualitatively, the Visicorder appeared to show two types of pressure rises. The apparent fastest rises were those shown by Runs B-3 and B-6, while Runs B-5, B-7, B-8 and B-10 showed slower rise times and generally lower pressure peaks. It appeared that there was a correlation between a significant production of CO_2 and CO, and a relatively non-reactive smelt.

Although it is recognized that more data are needed to firmly establish this point, it appears that the chemical reactions taking place have some effect on the apparent reactivity of the smelts investigated. Thus, the milder behavior of the latter runs mentioned above could be explained, because of the higher CO_2 and CO production, on the basis that the endothermic reaction

$$Na_2CO_3 + H_2O \rightleftharpoons 2NaOH + CO_2$$

takes place, thus slowing down, somewhat, the production of steam. It will be noted, as mentioned above, that these runs contained low hydroxide at the end of the run (and would be expected to be low in hydroxide at its beginning). From a chemical point of view, such low hydroxide levels would tend to favor the production of CO_2 and CO.

Elemental Sodium Formation

The question of whether elemental sodium exists in smelt and plays a part in the explosion mechanism has been raised many times.
While it was shown in our computer studies that sodium vapor could indeed exist in the highly reducing atmosphere of the smelt bed, the question remains whether sodium dissolves in smelt and exists in smelt in view of its boiling point of 1616 F.

In order to demonstrate experimentally whether sodium will form and

remain in molten smelt, a laboratory test has been devised. Briefly, a graphite capsule, containing Na_2S, Na_2CO_3 and carbon, will be heated in a vertical muffle furnace so that the smelt will be under a pressure of 10 psi of products from the reaction of the charge. The capsule will be quenched and sodium determined by hydrogen evolution at room temperature.

The graphite crucibles are being machined, and the test is scheduled to start September 7.

RECOVERY UNIT SHUTDOWN TESTS

The most desirable procedure for shutting down a Kraft-type recovery unit during a period of distress has been a topic of discussion throughout the industry for many years. The central theme of this discussion has focussed upon the question of whether residual quantities of active fuel and chemicals can be safely handled by the unit.

One factor which has been questioned is quenching of the bed with with limited quantities of partially volatile organic fuel after evaporation of H_2O and subsequent decrease in total air flow which might place the entire furnace, boiler, and auxiliary equipment into the fuel-rich region. Such a procedure was based, in part, on the philosophy that the furnace should be cooled as quickly as possible so that the pressure parts of the recovery unit would be protected. To date, this concern for the pressure parts of the unit has apparently outweighed the possibility of gaseous-type hazards that might arise.

B&W Progress Report No. 4 showed that large volumes of combustible gas were liberated from the thermal decomposition of black liquor solids and focussed attention on the possibility that the release of these gases constituted a potential hazard inherent in the present shutdown procedure. As

a result, a new approach to this problem was suggested and recommended for evaluation on a commercial unit. This new approach involves the following principles:

1. There is no quenching of the bed by black liquor.
2. Primary air flow is shut off.
3. The FD and ID fans are allowed to stay in operation; the unit is thereby kept on the air-rich side during the entire shutdown.

Test Program

The D. M. Bare Company which has a B&W 122 ton/day recovery unit (Figure 9) (PR-69) was equipped with a guillotine-type shut-off damper in the primary air duct of the furnace. A test was planned and executed on July 23, 1965.

Objectives. The objectives for the test were (1) to determine the rate of temperature depression in the bed and throughout the unit and (2) to determine variations in gas composition during a shutdown.

Sequence of Events. Data on the recovery unit were obtained prior to, during, and following the sequence of events listed below.

1. Assure that all auxiliary fuel is secured and unit is operating at normal mill rating.
2. Shut off black liquor flow to furnace.
3. Open tertiary air damper wide (individual port dampers open prior to test).
4. Shut off primary air by closing louver dampers.
5. Maintain total air flow equivalent to that which existed prior to closing primary air louver.
6. Close emergency trip damper in primary air duct. Maintain same total air flow.

b. Panel Board Data - In order to record other critical temperatures, pressures, flows, etc., 35 mm pictures of the entire panel board were taken in 5 second intervals. See Figure 11.

Preliminary Results

(1) Smelt and gas temperature in primary zone of the furnace did not drop off as rapidly as might be expected (see Figure 10). This could have been due to observed leakage of combustion air from the secondary to the primary windbox; thus the primary air possibly was never completely stopped.

(2) Assuming that a representative gas sample was obtained during the test, gas analysis at the furnace outlet (opposite nose) indicated that there were no danger periods of gaseous type explosive mixtures during the entire shutdown.

(3) The low gas temperature (see Figure 10) at the furnace nose indicates that possibly air channeling was taking place, thereby questioning in part result 2. The oxygen concentration at the boiler outlet should show values of 10%+ oxygen as soon as the shutdown commenced.

(4) The analysis of the smelt samples, carried out to determine whether chemical and/or physical changes were occurring, are in progress. Visually, significant differences were noted between cooled smelts as the shutdown proceeded. The smelt appeared to become denser (granite-like) at the end of the test.

(5) The shutdown was a smooth one -- no smelt rushes were observed. No rapid changes which might be classified as hazardous were discernible.

a. Sodium sulfate

b. Humidification

c. Na_2O - NaOH

EXPENDITURES

Expenditures through July 31, 1965 are as follows:

Labor plus overhead	$103,816
Material	18,082
Total	$121,898

A cost control chart is attached.

Submitted by: C. H. Anderson

C. H. Anderson
Research Chemist

CHA/djl

TABLE I

SUMMARY OF RESULTS OF PRESSURE VESSEL EXPERIMENTS

Run #	Charge	Temp. °F	H_2O cc	Visicorder P_{max} (psig)	Gas Yield % of H_2O Added			Analysis After Run	
					H_2	CO	CO_2	Na_2S	NaOH
B-1	Na_2CO_3	1650	1	6	3.1	15.1	22.5		
		1700	1	6	6.5	17.3	23.8	-	1.64%
B-2	Smelt A	1600	1	-	20.5	-	-		
		1570	1	4	28.6	4.4	-	20.7	14.3
B-3	Smelt A	1800	1	0	36.7	2.2	.9		
		1690	1/2	7	37.5	.6	.4	26.7	4.9
B-4	Smelt A	1910	1	6	54.9	7.85	.3	-	-
B-5	Smelt B	1605	1	3	23.2	1.5	3.1		
		1600	1	3	19.4	.9	3.2		
		1595	1	3	9.9	.9	2.3		
		1608	1*	5	18.5	.5	1.0	19.9	3.4
B-6	Smelt A	1590	1	0	25.1	.5	.75		
			1	5	24.9	.4	.1	32.2	2.4
B-7	Smelt A	1600	1	1.0	15.9	.7	6.7		
		1600	1	6.9	13.7	.6	3.9	35.3	.43
B-8	Smelt B	1600	1	4.2	11.4	.7	8.0		
		1600	1	4.6	11.6	.2	11.9	25.2	.66
B-9	Na_2CO_3	1600	1	6.0	1.9	1.1	15.2		
		1600	1	6.0	1.2	.9	17.6		
		1600	1	4.2	1.2	.4	9.8		
		1600	1	7.2	1.1	.5	5.2		
		1600	1	7.0	1.6	.5	4.2		
		1600	1	4.3	1.5	.2	3.9	-	4.4
B-10	Smelt B	1600	1**	3.1	21.4	1.0	6.0		
		1600	1**	3.0	20.2	.6	4.2		
		1600	1**	3.0	17.1	.2	2.5		
		1600	3**	8.1	12.5	.2	1.3	27.5	1.5

*10% Green Liquor

**Water injected on top of smelt.

TABLE II

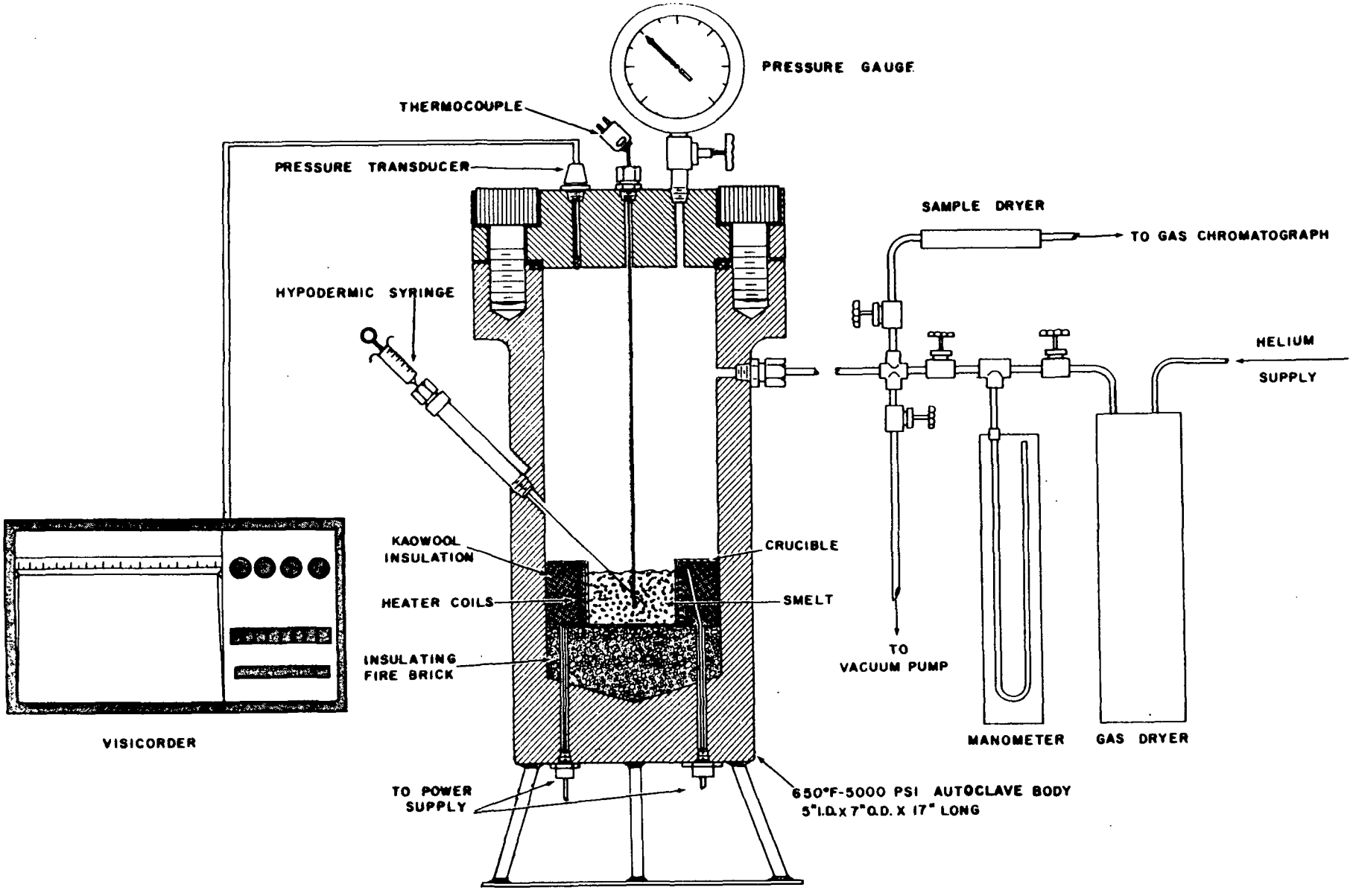
GAS ANALYSES AT FURNACE OUTLET

Time	Concentration % by Volume (Dry Basis)			
	O_2	CO_2	N_2	Combustible
Prior to Test[1]	7%	-	-	Nil
During Test[1]	>10%	-	-	Nil
2112[2]	-	-	-	Nil
2116 - 2120[3]	20.8	0.2	79.0	Nil
2125[2]	-	5.5	-	Nil
2129[2]	-	2.6	-	Nil
2121 - 2130[3]	18.8	2.2	79.0	Nil

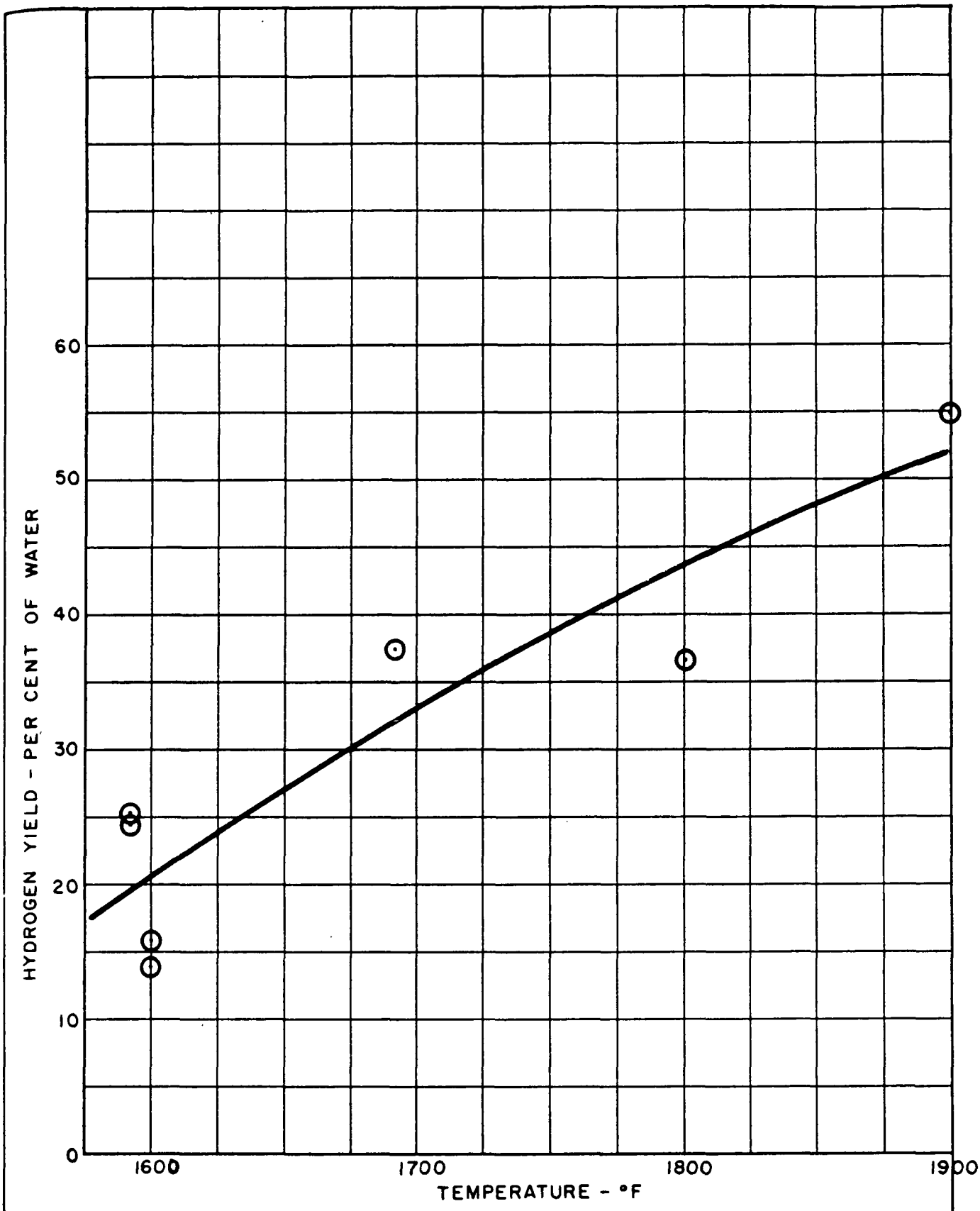
[1]Bailey Analyzer

[2]Gas Chromatograph (Field)

[3]Gas Chromatograph (Laboratory)

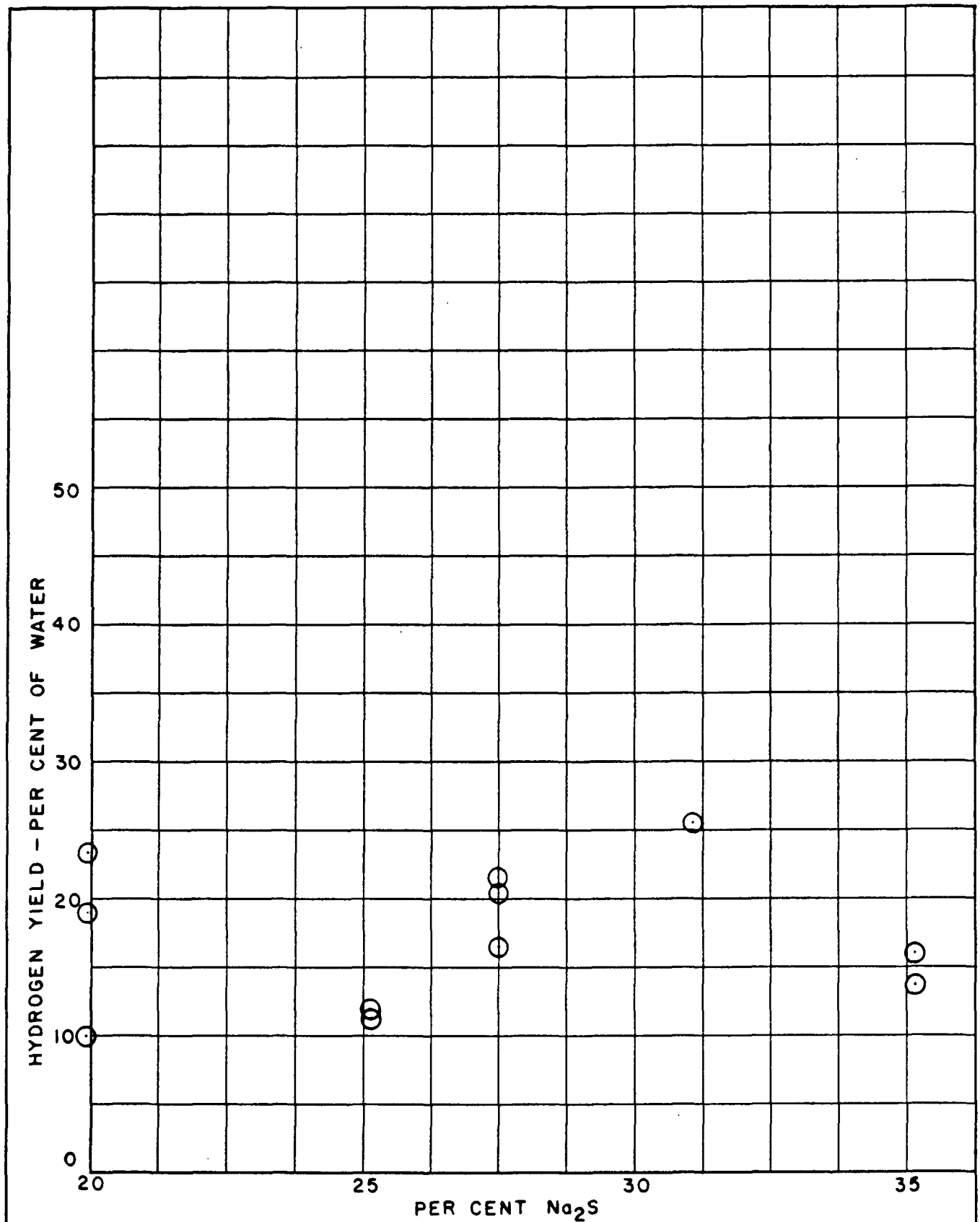


SCHEMATIC DRAWING OF EXPLOSION APPARATUS



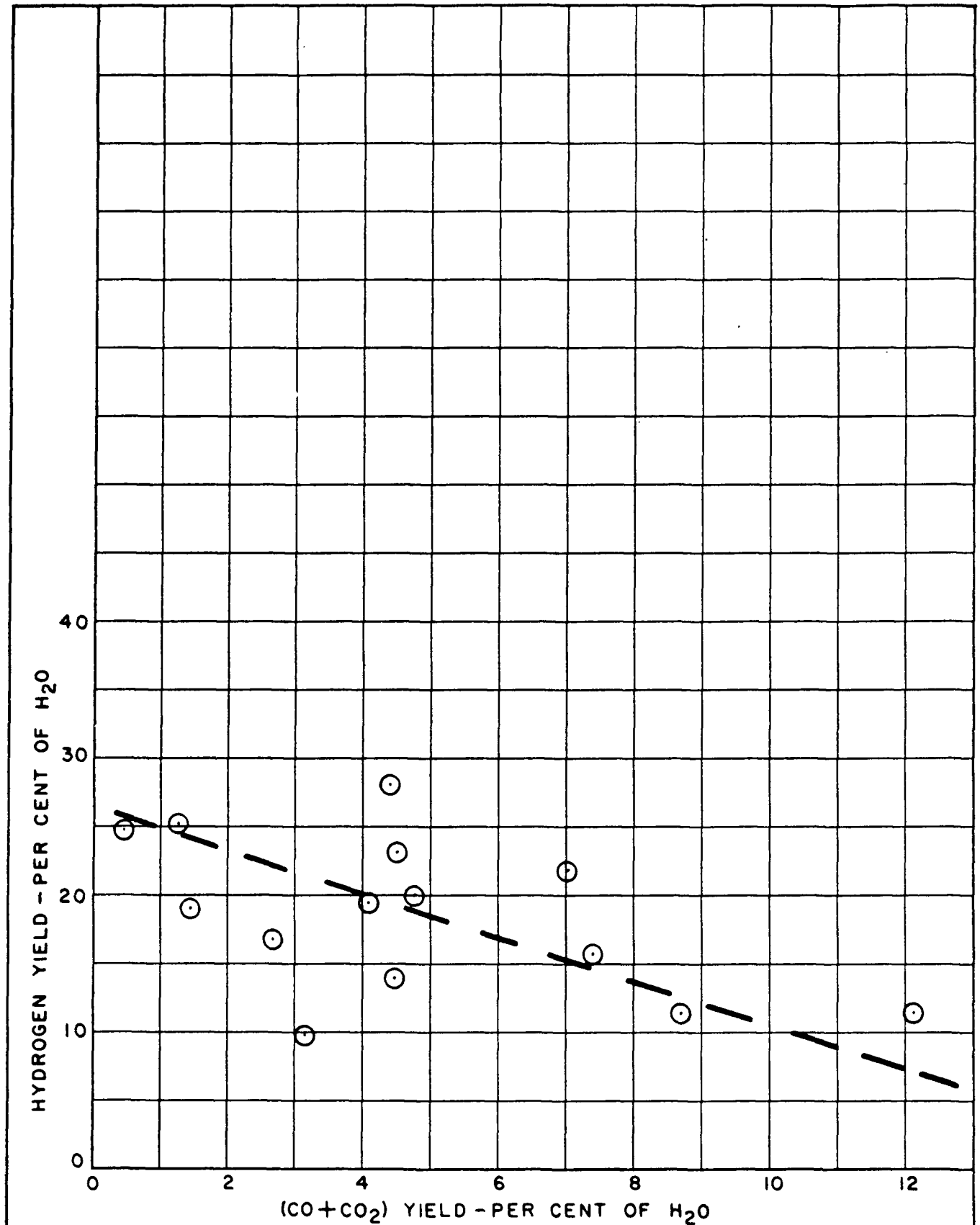
SUBJECT	HYDROGEN YIELD	FILE NO.	THE BABCOCK & WILCOX CO.
		BY	RESEARCH LABORATORY
	VS TEMPERATURE	DATE	ALLIANCE, OHIO
		REV.	DRAWING NO.

FIGURE 2



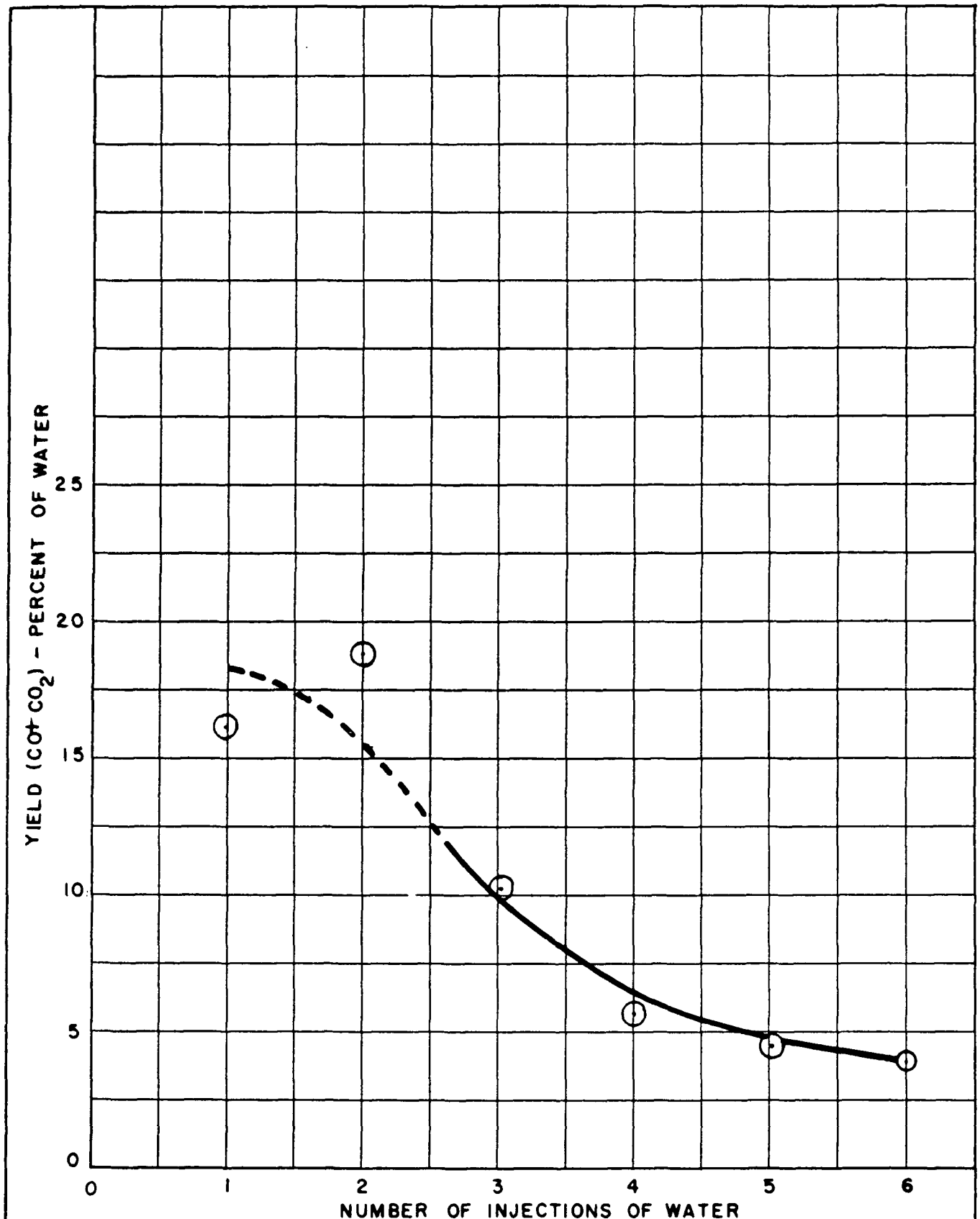
SUBJECT HYDROGEN YIELDS VS PER CENT Na_2S AS ANALYZED AFTER TEST (1600° ±5°F)	FILE NO.	THE BABCOCK & WILCOX CO. RESEARCH LABORATORY ALLIANCE, OHIO
	BY	
	DATE	
	REV.	DRAWING NO.

FIGURE 3



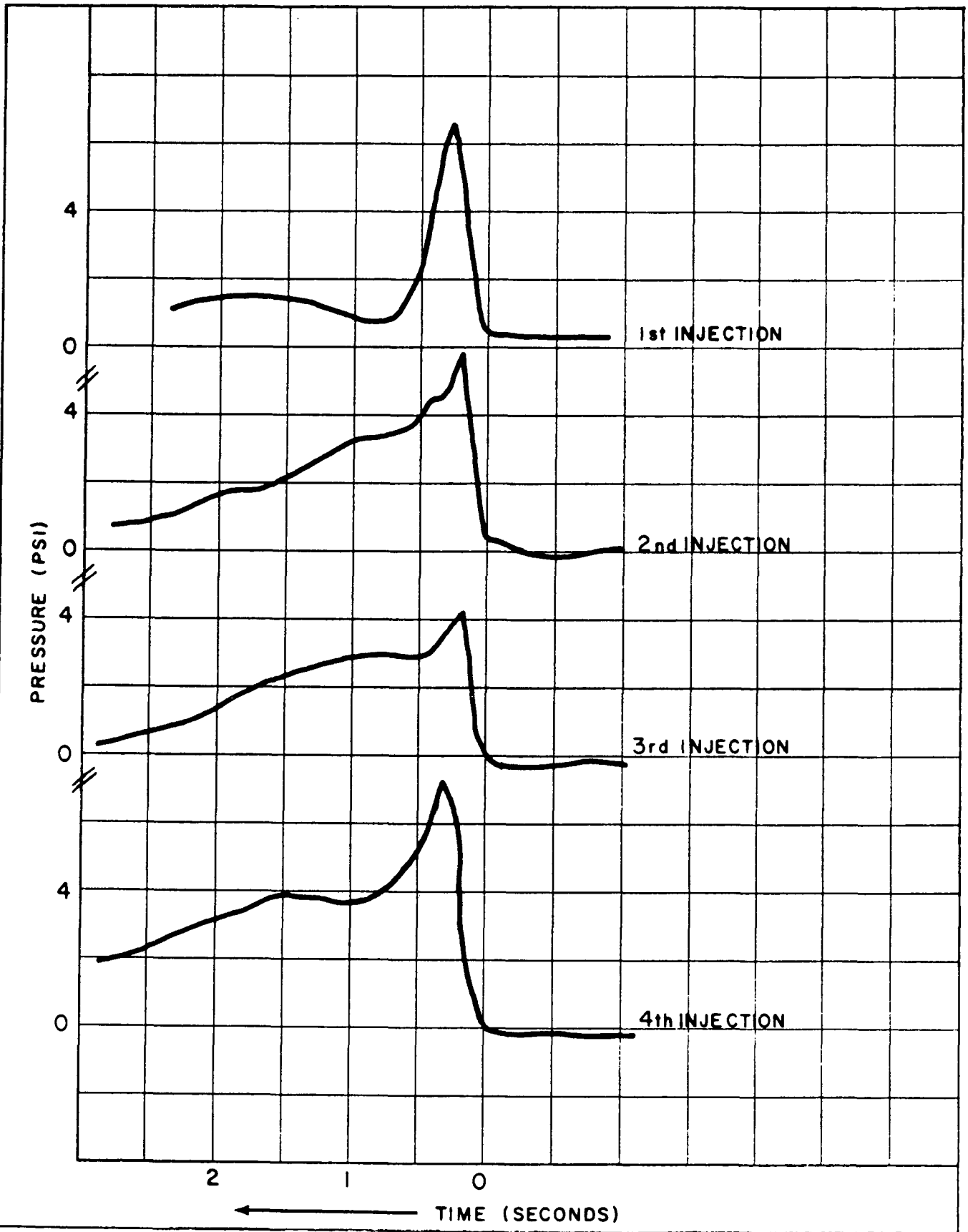
SUBJECT HYDROGEN YIELD VS $(CO+CO_2)$ YIELD. 1600°+5°F	FILE NO.	THE BABCOCK & WILCOX CO. RESEARCH LABORATORY ALLIANCE, OHIO
	BY	
	DATE	
	REV.	DRAWING NO.

FIGURE 4

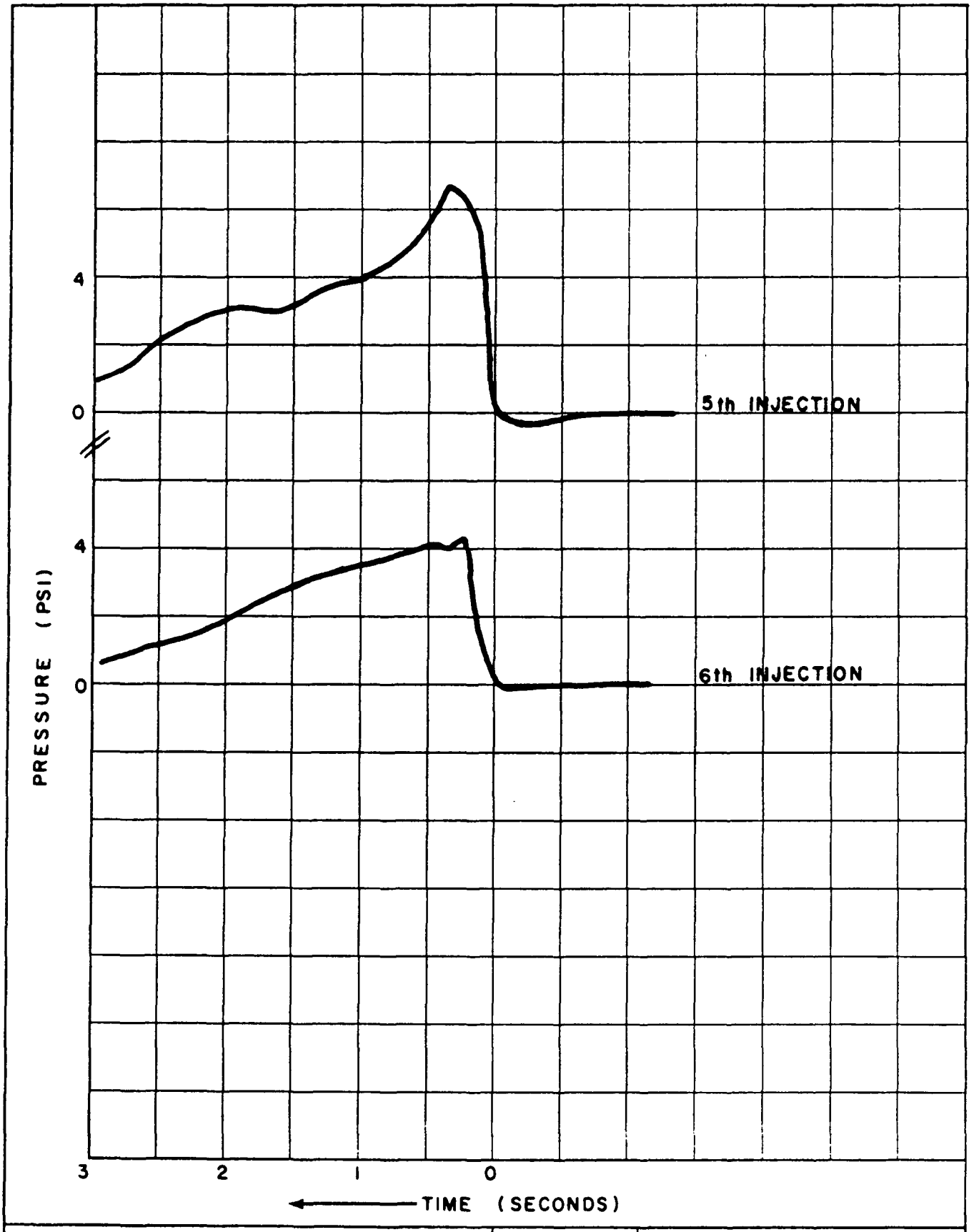


SUBJECT $(CO+CO_2)$ YIELD AS A FUNCTION OF SUCCESSIVE 1-CC INJECTIONS OF WATER IN Na_2CO_3 (1600°F)	FILE NO.	THE BABCOCK & WILCOX CO. RESEARCH LABORATORY ALLIANCE, OHIO
	BY	
	DATE	
	REV.	DRAWING NO

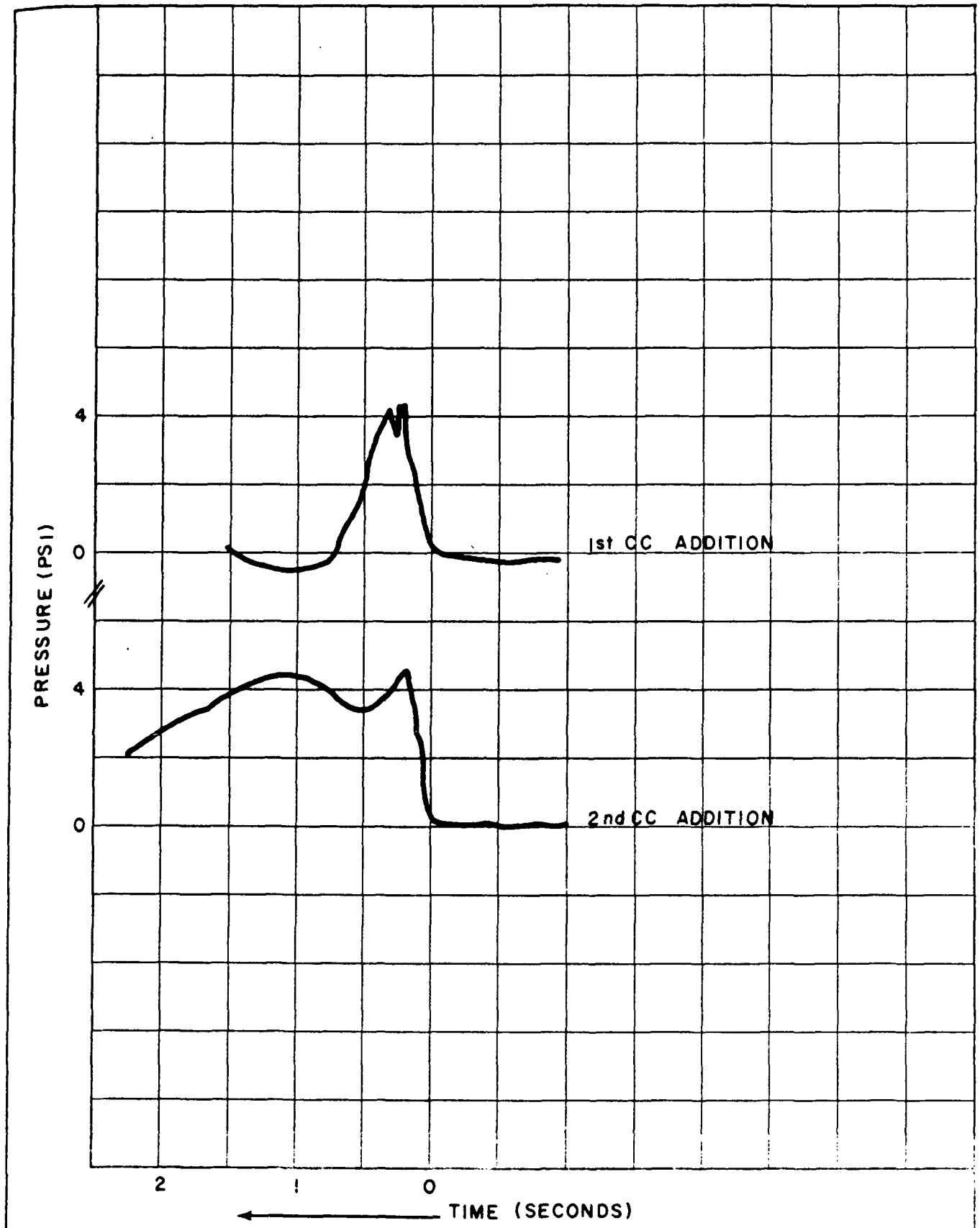
FIGURE 5



SUBJECT VISICORDER TRACINGS $Na_2CO_3 - H_2O$ REACTION	FILE NO.	THE BABCOCK & WILCOX CO.
	BY	RESEARCH LABORATORY
	DATE	ALLIANCE, OHIO
	REV.	DRAWING NO.

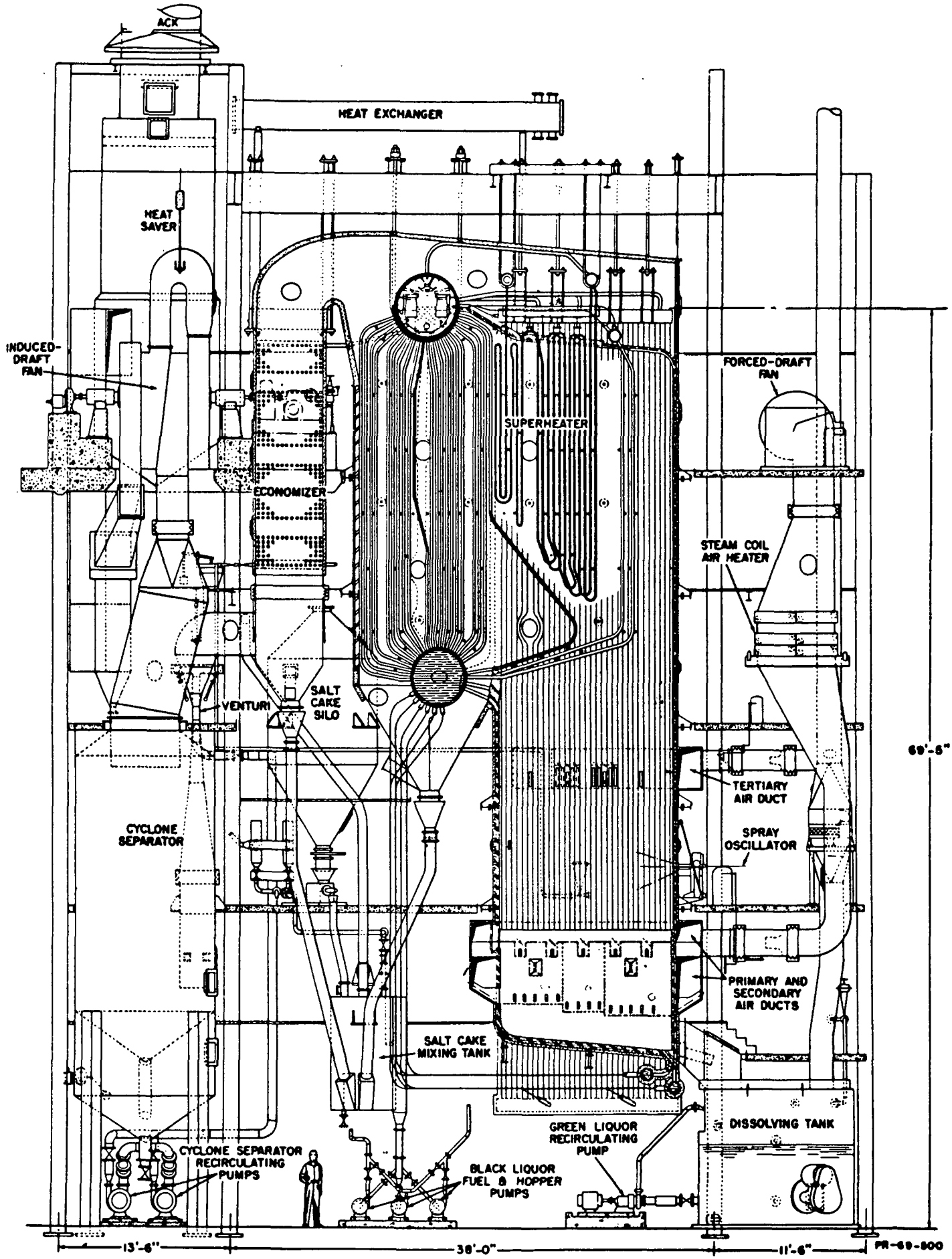


SUBJECT VISICORDER TRACINGS $Na_2CO_3 - H_2O$ REACTION	FILE NO.	THE BABCOCK & WILCOX CO. RESEARCH LABORATORY ALLIANCE OHIO
	BY	
	DATE	
	REV.	DRAWING NO.

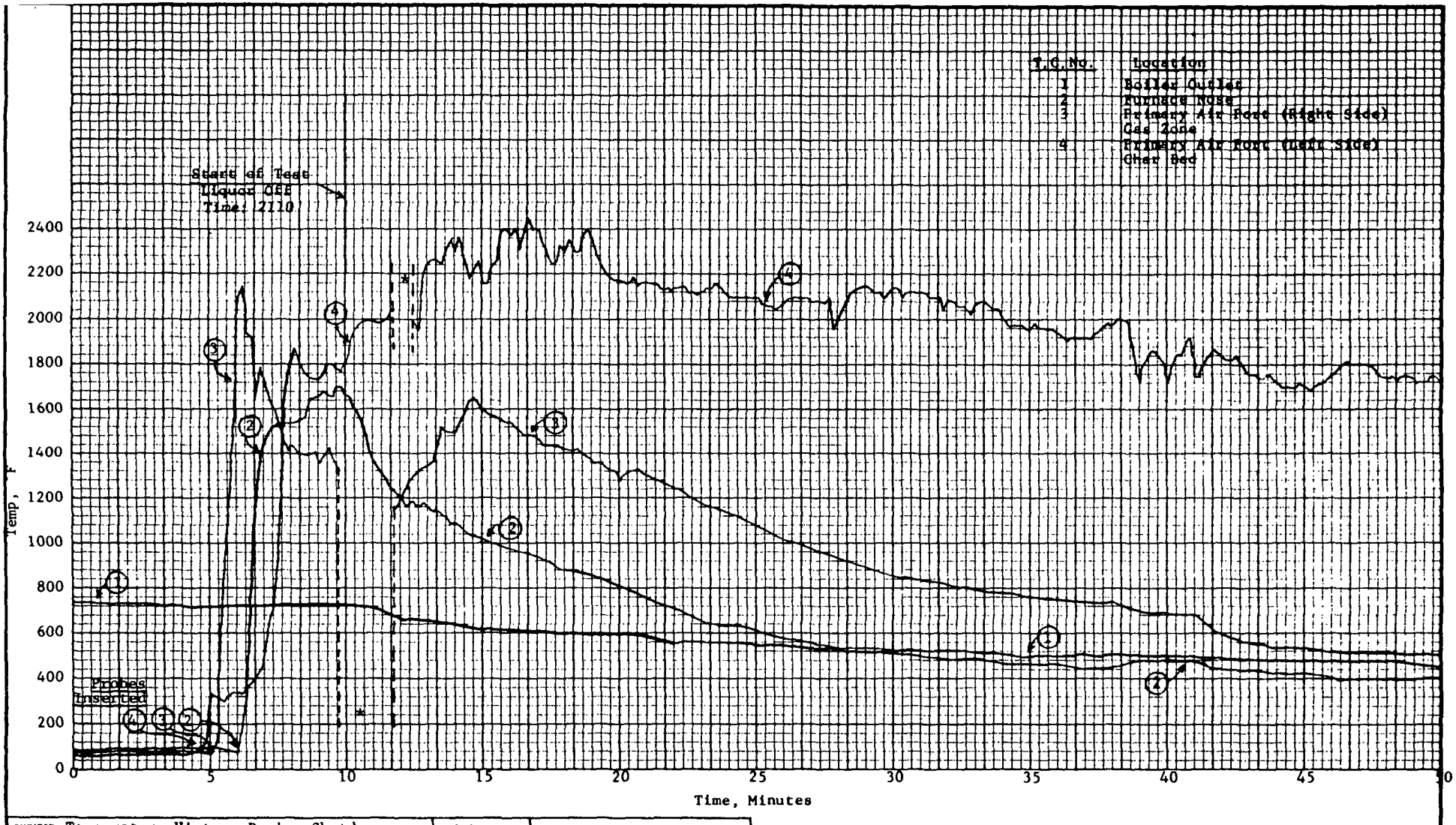


SUBJECT VISICORDER TRACINGS RUN B-8	FILE NO.	THE BABCOCK & WILCOX CO.
	BY	RESEARCH LABORATORY
	DATE	ALLIANCE, OHIO
	REV	DRAWING NO.

FIGURE 8



122 TON RECOVERY UNIT FOR
D. M. BARE PAPER COMPANY
ROARING SPRING, PENNSYLVANIA
B.&W. CONTRACT NO. PR-69

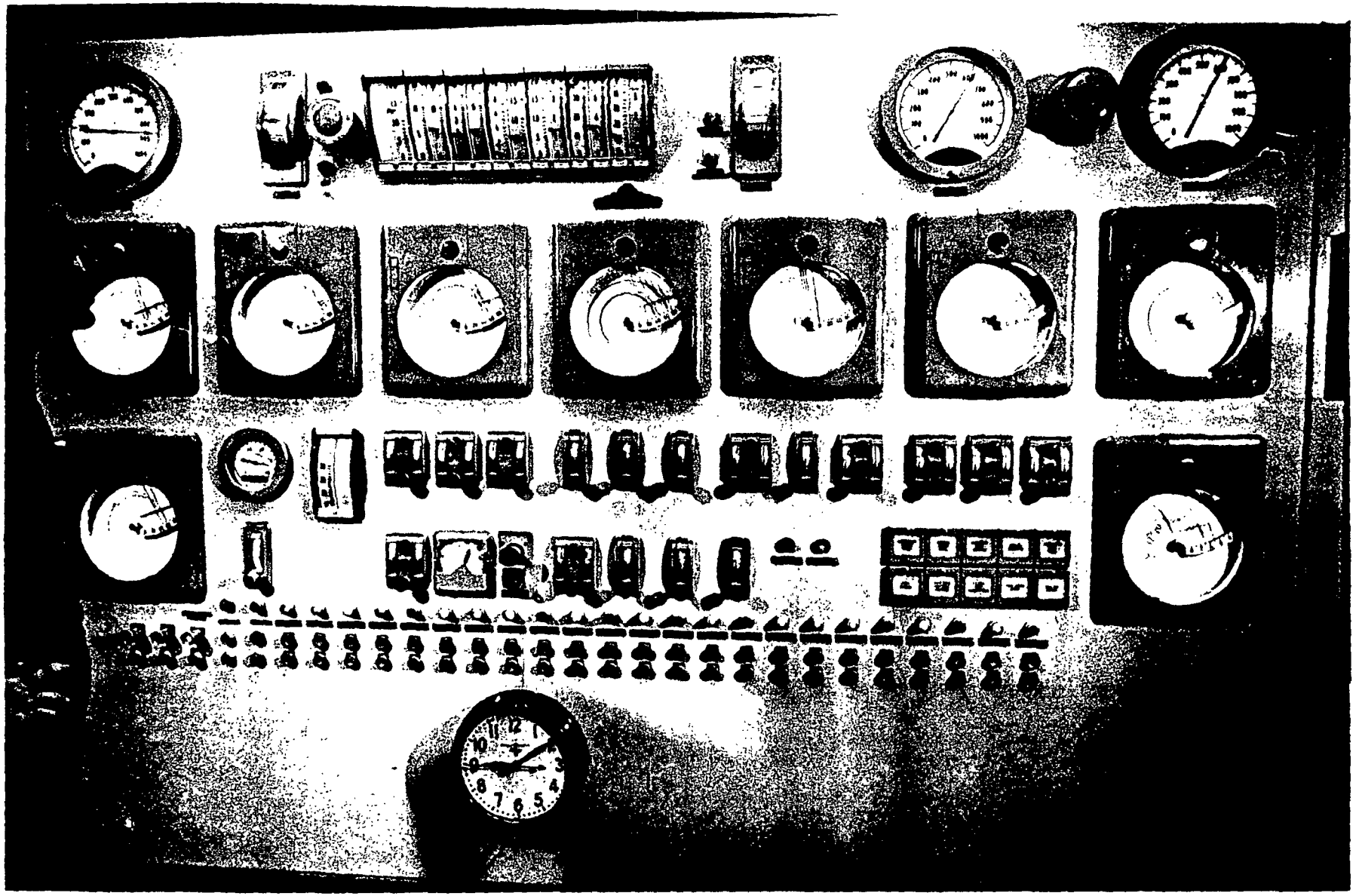


SUBJECT: Temperature History During Shutdown Test at D. M. Bare Paper Company	FILE NO.	THE BABCOCK & WILCOX CO. RESEARCH CENTER ALLIANCE, OHIO
	BY RAM	
	DATE 9-7-65	
Time 0 = 2100, July 23, 1965		DRAWING NO.

*Probes Removed from Unit

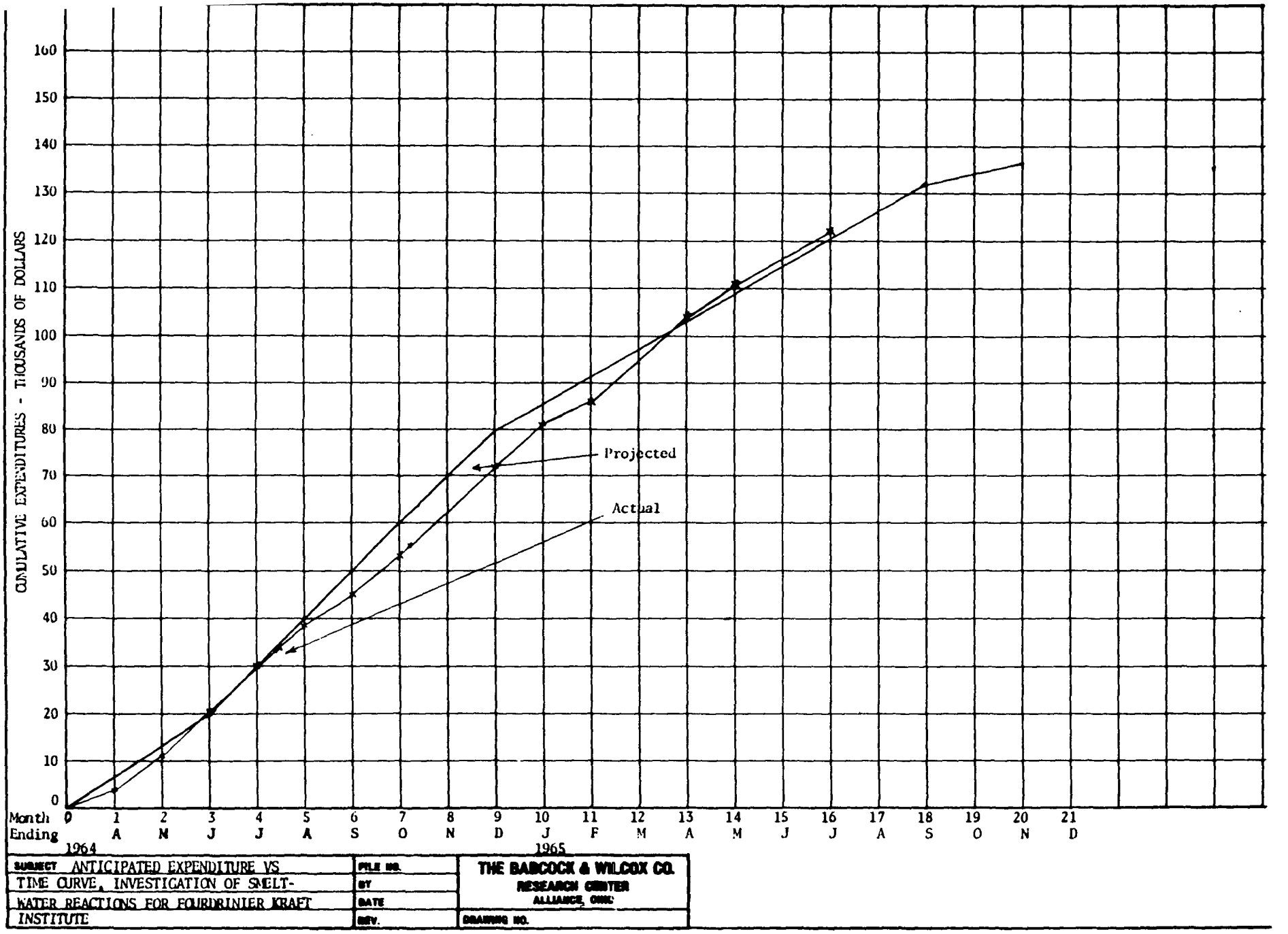
AL 98

K & E CO., NO. 10 8464 72330



TYPICAL PICTURE OF PANEL BOARD

FIGURE 11



SUBJECT ANTICIPATED EXPENDITURE VS TIME CURVE, INVESTIGATION OF SMELT-WATER REACTIONS FOR FOURDRINIER KRAFT INSTITUTE	FILE NO.	THE BABCOCK & WILCOX CO. RESEARCH CENTER ALLIANCE, OHIO
	BY	
	DATE	
	REV.	DRAWING NO.

TRIMONTHLY PROGRESS REPORT

Covering Work from June 6, 1965 through August 27, 1965

to

Dr. H. S. Gardner, Project Coordinator

The Institute of Paper Chemistry

Submitted by

Combustion Engineering, Inc.
Kreisinger Development Laboratory
Windsor, Connecticut

No. 6 Progress Report on The Combustion Engineering Program for Determining the Nature of and Remedies for Explosive Reaction(s) Between Smelt and Water in Kraft Chemical Recovery Furnaces

Introduction

The learning process almost invariably produces improvement in an initial theory as experimental work progresses. The development of the encapsulation mechanism theory is no exception. Ideas derived from the heat transfer study in Progress Report No. 5 have permitted changes in the encapsulation theory described in Progress Report No. 4 which make it fit the new information better.

The heat transfer calculations of C-E's No. 5 Progress Report showed that hot water and not steam would be contained in encapsulated water of 0.3 to 3.0 ml volumes after the 0.030 second average induction period for an explosion. A maximum temperature increase of only 60 °F would be realized in this period. The increased internal capsule pressure must then be due to thermal volumetric expansion of liquid water against the containment shell of frozen smelt. Pressure development during even this brief period could be substantial, ranging from 2000 to 6000 psi, as shown by Figure 3 of the heat transfer study.

Rupture of the shell would be a triggering mechanism for the explosive generation of steam produced when liquid water from the fragmented capsule meets molten smelt. The internal pressure developed in the capsule must serve principally to finely disperse the water and propel it at high velocity through the body of molten smelt once rupture occurs. The velocity of the water particles so produced would increase steam production rate by reducing the thickness of the external steam film on each water droplet. This film tends to impede heat transfer. The real explosion then would be due to the explosive generation of steam <u>after</u> capsule rupture placed its liquid water content in intimate contact with the molten smelt.

The tensile strength of the encapsulating shell necessary for an explosion would then have to be sufficient only to contain pressure high enough to effect proper subdivision and ejection velocity of water particles from the ruptured capsule.

The importance of encapsulation may be that it initiates a steam-forming physical explosion like a blasting cap initiates detonation of a chemical explosion of TNT. In each case, a small burst of energy may trigger the development of a much larger quantity of PV (pressure volume) energy from the rapidly expanding gases of the principal explosion.

It may be the case that capsule rupture and the explosive generation of steam from its small water content could initiate further mixing of smelt with "bulk" (non-encapsulated) water above on the surface of the smelt. Mixing of this larger volume of water with smelt would cause an even larger steam explosion.

Within the framework of this evolving physical explosion concept, our laboratory work during the period of this report was primarily concerned with two things:

1. Evaluation of the effect of extraneous sodium compounds other than Na_2S and Na_2CO_3 on the explosiveness of smelt.

2. Evaluation of possible safe quenching agents for the prevention of smelt explosions.

Four commercial recovery furnace explosions have occurred and been investigated by the writer (and others) since the initiation of this project. An attempt to relate pertinent explosion literature and project explosion consultants' opinions to the post-explosion evidence of the four explosions and to our laboratory work is appended to this report. (See Appendix).

Laboratory Experiments

a) Effect of sodium sulfate in smelt on explosive violence

The effect of Na_2SO_4 content of smelt on injection of water or aqueous solutions has been of considerable interest. Earlier work[1] had shown that a 2-10% concentration of Na_2SO_4 in smelt inhibited explosive violence in dissolving tank type quenches in which the smelt was poured into a large volume of water. A series of synthetic smelts of a wide range of sulfidity was made up from Na_2S and Na_2CO_3 to test the effect of Na_2SO_4 on water injection explosions. Each was melted rapidly in a graphite crucible so that reaction of Na_2SO_4 with the carbon crucible would be minimized. Gaseous CO is evolved vigorously by this reaction above about 1850 °F so initial smelt temperatures were kept below this level and the surface of the smelt was observed often to control the temperature. Analyses were made of several smelts which contained Na_2SO_4 before and after melting by the finally chosen procedure to assure that the melting technique did not convert appreciable Na_2SO_4 to Na_2S. Once 1800 °F smelt temperature was reached, the usual 3 ml. successive injections of room temperature water or water solution were made until either an explosion resulted or the smelt solidified. Results are shown in the appended Table 1.

Runs No. 1-3 indicated, as recognized from many previous tests, that Na_2S level must generally be above about 23% (approx. 30% TAPPI sulfidity) for water injections to cause explosions. (This limit was approximately 20% for dissolving tank explosions. However, the minimum % Na_2S for explosions with both kinds of smelt-water mixing is lowered significantly by presence of small percents of explosion intensifiers like NaCl or NaOH in the smelt as discussed further in section (c) or dissolved salts in the quench water.) Presence of 5.7 and 10% Na_2SO_4 did not alter this non-violent behavior as shown in Runs Nos. 2 and 3. Runs Nos. 4 and 5, however, showed that smelt below the threshold Na_2S content (approximately 20% Na_2S, 25% TAPPI sulfidity) containing 5% Na_2SO_4 exploded very violently when either 10% green liquor (10% smelt dissolved in water) or 10% sodium chloride was injected into the smelt. The fact that both NaCl and green liquor produced the same increase of explosive violence indicates that the Na_2S does not have a unique role in intensifying explosions. A better explanation for what appears to be a general property of dissolved salts seems to be the one in C-E

Progress Report No. 5, i.e., that stable salts dissolved in water decrease the life of the vapor blanket separating liquid water from hot smelt in a capsule. This increases heat transfer rate and hence, explosiveness. Explosions resulted from Runs Nos. 6 and 7. These four tests indicate that up to 10% Na_2SO_4 would be inadequate to inhibit explosive violence even in low sulfide smelt if it contacted green liquor formed by the dissolving of smelt by uncontrolled water in the furnace.

Runs Nos. 8 and 9 were made using a different kind of smelt composition. This was low sulfide smelt sensitized with 5% NaCl as might occur with smelt in a mill pulping salt-water borne logs. (Concentrations of up to 12% NaCl were found in the smelt from one such mill.) It exploded on addition of water by both injection and continuous stream addition. The latter term has been referred to as "simulated tube leak" in previous reports. Run No. 10 with this type of smelt containing 10% Na_2SO_4 as inhibitor also exploded, but mildly.

The next series of Runs, Nos. 11 to 16 was made to test Na_2SO_4 over a range of concentrations in moderate to high sulfide smelt (25%-37% TAPPI sulfidity) which is more explosive. All exploded, some very violently, on successive water injections even though Na_2SO_4 in 5.7 to 17.5% was present. Runs Nos. 12 to 16 smelts all lie in a range of Na_2S proportions in Na_2CO_3 which exploded violently without Na_2SO_4 in earlier experiments. Comparing Runs Nos. 1 and 11 indicates that a proportion of Na_2SO_4 high enough may even intensify explosive violence, rather than acting as smelt modifier to reduce explosive intensity.

Data in this Table prove within the limits of experimental procedure used, that sodium sulfate does not act as an explosion inhibitor on injection of either water or 10% water solutions of smelt or NaCl.

b) Effect of sodium hydroxide and sodium oxide in the smelt

A previous progress report by the Babcock and Wilcox research group suggests the possibility of an explosion caused by an exothermic reaction of water with Na_2O, if Na_2O is present in smelt. Because this suggestion implies a non- combustible explosion, a type of explosion of interest in the C-E program, experiments were conducted to indicate the extent to which Na_2O might be present in smelt, and the significance to explosions of the reaction between water and Na_2O.

The first series of experiments was arranged to test the effect of graphite crucibles on the formation of NaOH or Na_2O. A 450 gram batch of normal 28% Na_2S smelt was maintained molten at 1600°F and sampled after 15, 30 and 45 minute periods. (Fifteen minutes is the normal holding time on batches for C-E explosion experiments.) No NaOH, Na_2O or elemental sodium, which are grouped together by the TAPPI analysis method, was found by duplicate analyses on each of the three samples.

Another batch of 28% Na_2S smelt, prepared by the regular procedure, was heated in like manner to 1800°F in a graphite crucible. Here again no NaOH or Na_2O was found by analysis after heating for 15, 30 and 45 minutes. When maintained at 1800°F smelt temperature or below, graphite crucibles have not been found to modify the composition of smelt. Smelt melted in crucibles made of ZrO_2, iron, and graphite gave identical results in explosion tests with water injection. Graphite has

the advantage of being by far the most resistant material to corrosive attack of smelt found by C-E experimenters. Graphite is also cheap and readily available. It has excellent induction heating characteristics. Carbon is a material "native" to the chemical recovery furnace since it composes approximately 50% of char in the ash bed. These desirable attributes and the above experimental results confirm the choice of graphite as a crucible material for smelt explosion test studies.

Suppose Na_2O was produced in smelt by chemical reaction in a furnace bed. What effect would Na_2O have on the explosion behavior of the smelt when it contacted water? These and other questions were to be answered in the next series of experiments. A detailed analysis [1] of carefully taken and preserved samples of smelt from the spouts of 15 kraft mills operating under a wide variety of conditions was made by the writer about ten years ago. The maximum concentration of NaOH plus Na_2O and Na (if present) in any sample was 3.2% on one but the range of all other samples was 0.1 - 1.3%. If higher concentrations of these ingredients had been present in smelt in the furnaces, they must have been volatilized or changed by chemical reaction before reaching the smelt spout.

First, a small pea-sized quantity of pure Na_2O powder (95.7% by analysis) was dropped into about 100 ml. of room temperature water to gain some idea of the explosive violence of pure material on quenching. It combined with water by the following chemical reaction:

$$Na_2O + H_2O \text{ (gas)} \rightarrow 2NaOH + 44.7 \text{ Kcal (per mol of } Na_2O)$$

or

$$Na_2O + H_2O \text{ (liquid)} \rightarrow 2NaOH + 36.2 \text{ Kcal}$$

Samples of this size and three times as large produced a few bubbles and some warmth, but no real violence. Encouraged by these results we decided to proceed with explosion tests of Na_2O dissolved in a variety of melts. Repeated successive 3 ml. injections of room temperature water were made in each 450g batch of molten material at approximately 1800°F until it either solidified or an explosion resulted. Melting was done in graphite crucibles in the induction heating furnace by the usual technique. Results are shown in Table II.

Runs Nos. 1 to 3 were made with varying proportions of NaOH in Na_2CO_3. No concentration of NaOH in Na_2CO_3 produced explosions on injections of water into melts of these compositions. Even 100% NaOH did not explode. Runs Nos. 5 and 6 by contrast showed that 15% and 20% sodium chloride in Na_2CO_3 caused violent explosions. These data again emphasized that presence of sulfides is not required for an explosion.

Run No. 7 with 10% Na_2O in Na_2CO_3, which is about five times the normal level in plant smelt, did not explode on repeated water injections into the molten material. (The Na_2O in this and other experiments was quickly added to already molten 1600°F melt in order to avoid prior reaction with moisture from non-molten ingredients.) The 15% Na_2O in Na_2CO_3 of Run No. 8 exploded very violently. At this point it seemed that enough calibration runs had been made to indicate roughly the lower explosive limit for Na_2O in Na_2CO_3.

Runs Nos. 9 to 15 were made to compare the effect of Na_2O and NaOH in kraft smelt with that of NaCl. Run No. 9 showed again that 20% Na_2S smelt did not explode with repeated successive water injections. Neither were there explosions in Runs Nos. 10, 11, and 12 when 2% Na_2O. NaOH, and NaCl were added. The same kraft smelt containing 5% Na_2O exploded violently in Run No. 13, but 5% NaOH in Run No. 14 and 5% NaCl in Run No. 15 also sensitized the smelt and produced the same order of explosive violence.

It is concluded that neither Na_2O nor NaOH in concentrations normally found in smelt (up to about 2%) was sufficient to make 20% Na_2S smelt explode violently. Sodium chloride at 2% gave the same results. Sodium oxide at 5% in 20% Na_2S smelt sensitized it enough to produce violent explosions. Both 5% sodium hydroxide and 5% sodium chloride, however, produced the same violence as 5% sodium oxide in the same smelt.

From these experiments it appears that no unusual hazard would be presented by sodium oxide in kraft smelt at normal concentrations. At up to about four times the normal concentration, the effect of Na_2O was indistinguishable from that of the same proportion of NaCl or NaOH. Due to these results and the discovery that no detectable Na_2O, Na, or NaOH was created by the normal melting procedure for smelts in graphite crucibles, we feel that Na_2O, Na, and NaOH played no part in the violent smelt-water explosions under nitrogen atmosphere in the spherical test vessel which were described in the last C-E progress report.

c) Effect of sodium chloride combined with high sodium sulfide in smelt on explosion inhibition by quench solutions

Considerable attention has been devoted to aqueous quenching solutions because they still appear to offer the possibility for developing a safe commercially-feasible method for shutting down a recovery boiler rapidly should a water leak develop in the furnace. Results and discussion of experiments on quenching agents have been presented in the last four C-E progress reports.

Injection of quenching solutions into smelt has been used in most experiments because this method of mixing provides the most violent and consistent explosions with water. Thus injection represents the most drastic laboratory condition known for mixing smelt and water. If a quenching solution prevents explosions when injected into smelt under a wide variety of conditions, it is considered a good candidate for further study. But only after passing all tests without any kind of explosion would it be recommended for furnace testing.

Although 10% aqueous ammonium sulfate solution succeeded in inhibiting smelt explosions under a wide variety of simulated plant conditions described in the last progress report, it had not until recently been tried on high sulfidity smelt which contains sodium chloride, a smelt composition known from previous work to increase greatly the violence of smelt-water explosions.

A series of smelt compositions containing high Na_2S content, above about 23%, was made up to contain NaCl. A succession of 3 ml. injections of water or aqueous solution was made into each molten 1800°F

smelt until an explosion or solidification of smelt resulted. The outcome of these experiments is reported in Table III. Run No. 1 showed that high sulfidity smelt with 5% NaCl explodes violently on water injection. (It does also without NaCl). Run No. 2 confirmed previous data of C-E Progress Report No. 5 in illustrating that explosions with low sulfide smelt containing 5% NaCl are inhibited successfully by 10% ammonium sulfate solution.

Runs Nos. 3, 4 and 5, however, showed that the combination of high sulfide with even 1% NaCl was not inhibited by 10% ammonium sulfate, the most promising candidate developed to that time. Runs Nos. 6 and 7 (the latter run in duplicate) on the new standard smelt with high sulfide and 5% NaCl showed that 10% ammonium bicarbonate did act as an inhibitor where 10% ammonium sulfate had failed. It was reasoned that this contrasting behavior might be due to the difference in rate at which the two compounds form a vapor blanket on contact with hot smelt. (Chloride-containing smelt may be able to develop more rapidly an encapsulation shell strong enough to allow build-up of water-dispersing pressure since it is believed to be a stronger per unit thickness than smelt which contains no chlorides.) Runs Nos. 8 and 9 were hence made with ammonium hydroxide which has a high vapor pressure at relatively low temperature. The 9% (by weight as NH_3) ammonium hydroxide solution did successfully inhibit explosions but, like ammonium bicarbonate, it might pose in-plant problems due to lack of stability on storage. Runs Nos. 10 and 11 showed that almost the same concentration of ammonium hydroxide would be necessary when combined with 10% ammonium sulfate solution.

Next it was decided to try the effect of increased concentrations of ammonium sulfate in water solution. The 15% concentration at room temperature in duplicate runs No. 12 inhibited explosions with chloride-containing smelt. When chilled to 40°F in Run No. 13, however, it gave a mild explosion probably due to the decreased rate of ammonia vapor production. Chilling was used to approximate conditions of use in a plant with outdoor storage of quench solution. Further increase in concentration to 20% at room temperature in Run No. 14 inhibited explosions in duplicate experiments. At this point it was reasoned that the safest ammonium sulfate solution to use in a furnace would be the one capable of safe quenching after greatest dilution with boiler water from a tube leak. A forty per cent solution, which is the limit of solubility of this salt at 32 °F, was chosen for further tests. Run No. 15 at room temperature and No. 16 at 212°F, showed that 40% $(NH_4)_2SO_4$ successfully inhibited explosions over this temperature range.

Run No. 17 showed that 40% solution worked even with 10% NaCl dissolved in the smelt. Runs Nos. 18 and 19 showed that 40% solution also was effective at 140°F and 32°F. Runs Nos. 20 and 21 showed that 40% solution successfully inhibited the most violent quenching smelt to date (with 10 and 15% NaCl, and high sulfide) even when the solution was chilled to 36-38°F before injection.

It would seem in tests to date that 40% ammonium sulfate could inhibit any plant smelt composition with which we are familiar. More tests under a wide variety of simulated furnace conditions, however, must be run before a definite recommendation can be made.

d) Effect of anion type in quench solutions

It was a natural point of curiosity to wonder if some other ammonium compound or gas-producing chemical would inhibit explosions better than ammonium sulfate. A series of previously untried compounds was made up in water solution and injected in 3 ml increments into very high sulfide smelt with no chloride by the standard test procedure used in other experiments. Results are shown in Table IV.

The 10% ammonium sulfate solution successfully inhibited explosions, while 5% produced a surge showing border-line effectiveness. The 5% NH_4Cl of Run No. 4, by contrast with 5% $(NH_4)_2SO_4$, gave a violent explosion. The 10% NH_4Cl of Run No. 5 gave a mild explosion as did also Run No. 6 with 10% NH_4Br, another halide. All halides tried to date in either the smelt or in quenching solutions have increased explosion violence. Ammonium acetate in Run No. 7 was an effective inhibitor. It has poor stability on exposure to air and offers no known advantage over $(NH_4)_2SO_4$. In Run No. 8 the 10% ammonium bisulfate solution, which had a strongly acid reaction in water, was also effective. This suggested that dilute sulfuric acid might also work since it would generate gases (CO_2 and H_2S) on contact with smelt. Such was the case if the acid were strong enough as demonstrated in Runs Nos. 10 and 11.

At present no advantage of acid solutions is recognized. Storage and transfer to the furnace might cause corrosion problems. Pure ammonium sulfate in 10% solution is slightly acid with a pH of 6.0. In another experiment not shown in this table, the addition of enough sulfuric acid to adjust the pH of 10% $(NH_4)_2SO_4$ to 3.3 (as might occur with impure commercial grade material) did not decrease its effectiveness. Buffering ammonium sulfate solution with enough ammonia to put it on the alkaline side, about pH 9, would protect the tanks and lines from corrosion. This small proportion of free NH_4OH would be expected to slightly increase explosion inhibition.

Run No. 12 with 5% ammonium sulfamate, $NH_4SO_3NH_2$, a fire retardant material with high thermal decomposition point, 320°F, did not work and neither did urea in Run No. 14 which decomposes above 270°F. The 10% sodium sulfate solution of Run No. 13 caused an explosion. This agrees with the analysis of a furnace explosion reviewed by the writer in which salt cake in water solution (rather than in black liquor) had been sprayed into the furnace bed. The 10% ammonium bicarbonate inhibited explosions in duplicate Runs Nos. 15 and 16. It has a high gas-producing capacity but is thermally unstable in dry form and specially in aqueous solution. The dibasic ammonium citrate was a successful inhibitor at either 10% or 5% in Runs Nos. 17 and 18 but has the disadvantage (compared with ammonium sulfate) of less stability and more cost.

To date there appear to be three serious candidates for further study: ammonium sulfate, ammonium hydroxide, and ammonium bicarbonate. We are concerned that the latter two solutions applied to the ash bed and smelt in a furnace may have too much volatility of active ingredient, i.e., that they may lose gas supply too rapidly on contact with hot furnace gases or alkaline char to retain enough for safe quenching of molten smelt below, which is the real problem. Only further testing can establish whether this is a valid criticism.

Discussion of Quenching Agents

How much quenching solution would be necessary to cool the molten smelt to a safe temperature in a 20' x 16' 300 ton C-E decanting bottom furnace? Mr. L. J. Jacobs of C-E made a number of assumptions in performing the following calculation. For instance, the sensible heat content of the ash bed was disregarded. A 3.82" depth of molten smelt was assumed over the entire bottom of the furnace. Furnace hearth dimensions of 19' 5/8" x 15' 9 5/8" were taken to correspond with an actual contract. The smelt would be cooled only to the solidification point, 1430°F. This would require approximately 263 gallons of aqueous quench solution or 2200 lb, assuming heat removal was not affected by the dissolved $(NH_4)_2SO_4$. The water of the solution would generate about 60,000 ft^3 of steam at 212-F which would be expected to provide an inert atmosphere for combustion reactions, especially in the bottom of the furnace. Chemical reactions in the bed like pyrolysis of black liquor and the water gas reaction would probably be quenched speedily by spraying liquid water solution on the bed, since aqueous solutions have a high heat capacity.

What makes some aqueous chemical solutions non-explosive on injection into molten smelt? The answer seems to lie in their ability to create large volumes of gas quickly on contacting smelt. The gas production necessary for a successful aqueous quenching agent can come from several types of reactions: (a) the production of vapor by volatilization of a high vapor pressure material like ammonium hydroxide, volatile compounds like acetone and methyl alcohol, or even hot water above 187°F. (b) the chemical reaction of smelt with aqueous solutions like dilute sulfuric acid (to give CO_2 and H_2S) or ammonium sulfate (to give ammonia) or (c) the thermal decomposition of compounds like ammonium bicarbonate (which yields H_2O, CO_2, and NH_3).

The gas blanket provided inside the capsule by such quenching agents is believed to decrease the rate of heat transfer from the molten smelt to water inside the capsule and hence also the thickness of the surrounding frozen smelt and the temperature of the encapsulated water. In addition we believe this gas blanket provides a compressible volume inside the shell which is able to absorb thermal expansion of the encapsulated liquid water without great increase in internal capsule pressure. The presence of this enveloping gas film around the enclosed volume of water would thus decrease the chance of an explosive encapsulation. A vapor blanket would decrease the build-up of water-atomizing pressure if a water-containing capsule did form and rupture.

Quenching agent candidates can now be chosen easier since several tentative criteria have been established which simplify selection. For instance, a quenching agent ideally should: (1) generate large volumes of non-flammable, non-toxic gas readily on rapid heating in aqueous solution below 212°F or on chemical reaction with smelt, (2) have sufficient stability in aqueous solution to allow long-term storage in metal tanks over a range of temperatures normal to in-plant and outdoor conditions, (3) leave no residue on application to smelt which will contaminate the the chemical recovery system, (4) be highly soluble in water, and (5) be cheap, non-toxic, stable on storage in solid form, non-corrosive, and readily available in commercial quantities. Some of these qualifications can obviously be sacrificed if the material is an effective enough inhibitor.

Future Work

Work in the final four months of the project in 1965 will concentrate primarily on the development of practical remedies for smelt explosions in furnaces. The mechanism studies have provided several clues to measures which could possibly prevent explosions in the field. Areas to be covered include the following:

1) The application of aqueous quench solutions to the smelt and ash bed as soon as a tube leak is discovered. (A good automatic system for leak detection would add considerable utility to this system.) The three candidates mentioned earlier, ammonium sulfate, ammonium bicarbonate, and ammonium hydroxide will be screened extensively by tests which simulate a wide variety of furnace conditions. Some of the variables to be studied are the effect of smelt composition (Na_2S, NaOH, and NaCl), presence of ash bed and black liquor, tests on samples of plant smelt from several mills, method of addition of quench solution, and a detailed analysis of decomposition products, both gases and solids. Additional quenching agents will be screened concurrently as they come to our attention.

2) The tendency of black liquor itself to explode physically in contact with smelt will be explored more thoroughly above the 35% maximum solids concentration which exploded in previous tests. New means of injecting heavy liquors will be tried in order to determine more exactly the upper concentration (and inorganic salt content) which can explode under the best possible mixing conditions. The effect of strong black liquor applied to the surface of smelt on cooling rate and accessibility to water will also be studied.

3) A limited additional number of smelt additives to modify its explosiveness on contact with water will be tried. Fifteen are on hand ready for testing.

4) A scale up of water quantities from 5 ml. maximum at present in the plywood booth to 50 or 100 ml should be made in the spherical vessel in order to get a better idea of the pressure signature of larger explosions more characteristic of those in an operating furnace. Such data would be useful in the stress analysis study of furnace explosions being made by Mr. R. Robinson at Illinois Institute of Technology Research Institute.

Completion of these additional studies should allow us to make definite recommendations about remedial measures worthy of study in a black liquor-fired semi or full scale furnace. This may be the next step beyond the present research contract.

Conclusions

(1) Under proper circumstances molten smelt can react physically with submerged liquid water very rapidly to produce steam explosively.

(2) Sodium sulfate in the smelt does not inhibit physical smelt-water explosions.

(3) The normal procedure for preparing experimental smelt in graphite crucibles does not produce significant quantities of Na_2O, NaOH, or elemental sodium.

(4) The presence of Na_2O, NaOH, or NaCl in laboratory smelts results in equivalent behavior on contact with water indicating that no unusual explosive contribution is to be expected from the presence of Na_2O.

(5) High sulfide smelt (above about 25% Na_2S) with sodium chloride is a particularly explosive composition hard to inhibit by quenching solutions. The 40% ammonium sulfate solution in water, either hot or cold, successfully quenched high sulfide-chloride smelts. More work on this and other quenching solutions will be necessary before a recommendation for plant trial can be made.

Expenditures on the C-E Smelt-Water Explosion Study

Costs (cumulative) of the Combustion Engineering, Inc. study as of July 31, 1965 are itemized as follows:

Labor	$ 36,950
Overhead	57,050
Materials	47,200
Total	$142,000

A graph showing the rate of expenditure is appended.

WHARTON NELSON
Senior Project Engineer

CHARLES L. NORTON
Research Engineer

August 28, 1965

TABLE 1

Effect of Na_2SO_4 in Smelt

	% Na_2S	Other	% Na_2SO_4	Quench Solution	Explosion
1.	22.9			Water	None
2.	17.9		5.7	Water	None
3.	16.9		10	Water	None
4.	19.7		5	10% Green Liquor	V*
5.	19.9		5	10% NaCl	V*
6.	20.6		10	10% Green Liquor	V*
7.	16.5		5	10% NaCl	Moderate
8.	20.4	5NaCl		Water	V*
9.	19.3	5NaCl		Continuous stream addition	Moderate
10.	17.2	5NaCl	10	Water	Mild
11.	21.4		17.4	Water	V*
12.	25.9		5.7	Water	Moderate
13.	25.3		10	Water	V*
14.	25.4		9.1	Water	Mild
15.	27.5		6.1	Water	VV*
16.	30.1		17.5	Water	V*

* Crucible shattered by explosion
V is volent
VV is very violent

TABLE II

Effect of NaOH, NaCl, and Na_2O in Melts
(3 ml. injections of water were used in each case)

	Melt, % Compostion	Explosion
1.	15 NaOH - 85 Na_2CO_3	Surge
2.	20 NaOH - 80 Na_2CO_3	None
3.	50 NaOH - 50 Na_2CO_3	Pops
4.	100 NaOH	Violent Spitting
5.	15 NaCl - 85 Na_2CO_3	V
6.	20 NaCl - 80 Na_2CO_3	V
7.	10 Na_2O - 90 Na_2CO_3	None
8.	15 Na_2O - 85 Na_2CO_3	VV*
9.	20% Na_2S smelt	None
10.	2 Na_2O - 20% Na_2S smelt	None
11.	2 NaOH - 20% Na_2S smelt	None
12.	2 NaCl - 20% Na_2S smelt	None
13.	5 Na_2O - 20% Na_2S smelt	V*
14.	5 NaOH - 20% Na_2S smelt	V*
15.	5 NaCl - 20% Na_2S smelt	V*

* Cruicible shattered by explosion
V is violent
VV is very violent

TABLE III

Effect of NaCl and High Sulfidity on Inhibition

Runs	% Na_2S	% NaCl	Injections **(3 ml)	Explosion
1.	28.1	5	Water	VV*
2.	18.5	5	10% $(NH_4)_2SO_4$	None
3.	26.4	5	"	V*
4.	25	3	"	V*
5.	25	1	"	VV*
6.	27.8	5	5% NH_4HCO_3	V*
7.	25,27.2	5	10% NH_4HCO_3	None
8.	25.7	5	4.5% NH_4OH	V*
9.	27.9	5	9%NH_4OH	None
10.	25	5	10% $(NH_4)_2SO_4$, 3% NH_4OH	Moderate*
11.	25	5	10% $(NH_4)_2SO_4$, 9% NH_4OH	None
12.	25,25	5	15% $(NH_4)_2SO_4$	None
13.	28.2	5	40°F 15% $(NH_4)_2SO_4$	Mild*
14.	27.3,25	5	20% $(NH_4)_2SO_4$	None
15.	27.0	5	40% $(NH_4)_2SO_4$	None
16.	26.6,27.5	5	212°F 40% $(NH_4)_2SO_4$	None
17.	27.1	10	40% $(NH_4)_2$ SO_4	None
18.	28.2	5	140°F 40% $(NH_4)_2SO_4$	None
19.	25.7	5	32°F 40% "	None
20.	26.6	10	36°F 40% "	None
21.	25.8	15	38°F 40% "	None

* Shattered crucible
** Made with room temp.(80°F) solution unless stated otherwise.

TABLE IV

EFFECT OF ANION

Run	% Na_2S Smelt	Aqueous Quench Solution	Explosion
1	30	5% $(NH_4)_2SO_4$	Surge
2	"	10% "	None
3	"	" "	None
4	"	5% NH_4Cl	V*
5	"	10% "	Mild
6	"	10% NH_4Br	Mild
7	"	10% NH_4 Acetate	None
8	"	10% NH_4HSO_4	None
9	"	"	None
10	"	0.5% H_2SO_4 (N/10)	Mild
11	"	5% H_2SO_4	None
12	"	5% NH_4 Sulfamate ($NH_4SO_3NH_2$)	Mild
13	"	10% Na_2SO_4	Mild
14	"	10% Urea $(NH_2)_2CO$	VV*
15	"	10% NH_4HCO_3	None
16	"	"	None
17	"	10% Dibasic NH_4 citrate	None
18	"	5% Dibasic NH_4 citrate	None

* Shattered Crucible
V is violent
VV is very violent

APPENDIX

Preliminary Analysis of Recovery Furnace Explosion Damage

(a) Shock waves developed by smelt-water explosions

A chemical reaction to be explosive must have three characteristics[2]. The heat of reaction is a criterion of the efficiency of the explosive material and is its most important characteristic. Thus a chemical reaction must be highly exothermic to be explosive in nature. Second, it must take place at a high rate, which distinguishes normal chemical reactions from explosive ones. Finally, a chemical reaction must form a gas. For instance, the following well-known thermite reaction is rapid and highly exothermic, but does not form a gas. It hence does not explode.

$$2Al + Fe_2O_3 \longrightarrow Al_2O_3 + 2Fe + 198Kcal \ (99Kcal/mol \text{ of } Al)$$

It can therefore be concluded that only the simultaneous combination of these three basic factors: exothermicity, high process rate, and gas formation, can guarantee a chemical type explosion.

Higgins and Schultz[3], in their thorough study of molten metal-water interactions which might take place in case of a run-away nuclear reactor, described a number of interesting results which seem to contrast with those from the present study. They mixed intimately the molten metals, uranium, zirconium, aluminum, sodium-potassium alloy, and stainless steel with water under various conditions and recorded the pressure waves and other variables in a highly instrumented system. Mixing was accomplished by spraying the molten metals into water and also by finely dispersing molten metal submerged in water with a blasting cap. With the two methods of mixing, the results were equivalent when particle-size distribution was approximately the same.

Higgins and Schultz state that the chemical reaction of molten aluminum with water (which occurs if the metal is very hot and finely divided) is highly exothermic and produces hydrogen, and that the reaction is nil up to 2138°F. (The melting point of aluminum is 1220°F.)

$$2Al + 3H_2O \longrightarrow Al_2O_3 + 3H_2 + 160Kcal (80Kcal/mol \text{ of } Al)$$

The proportion of aluminum reacting with water (approx. 60%) was higher than for other metals tested.

Higgins and Schultz recorded the pressure rise times on oscillograms (reproduced as Figure 1). To quote them:

> "The pressure pulses measured in the explosion dynamometer were primarily due to the liberation and expansion of the hot hydrogen gas.....
>
> "In observing the pressure rise time, it is evident that the

> metal-water reactions are not high-order explosions -- taking milliseconds rather than microseconds to attain peak pressure. The metal-water reactions could be described as deflagrations instead of detonations, but are slightly more brisant than black powder, as indicated by the rates of pressure rise..... From the above considerations and from the absence of shattering-type damage, it was concluded that the effect of shock waves was not important in these tests."

Contrast these rates of chemical reaction of molten metals and water with the pressure signature (pressure versus time trace) of a typical C.E. laboratory smelt-water physical explosion reproduced as Figure 2. It can readily be seen that physical smelt-water explosions: (1) average 0.1 to 3 milliseconds and are hence 5 to 300 times faster, (2) have much faster rise and decay times, and (3) are of an entirely different type from deflagrating chemical reactions of molten metals with water. The wave from a smelt-water explosion by contrast is a shock wave produced from explosively-generated steam. This concept is discussed in more detail in the section which follows.

The violent smelt-water explosions in nitrogen atmosphere described in C.E. Progress Report No. 5 ruled out combustion as an explanation for these laboratory explosions.

(b) Inspection of four explosions

The distribution of damage in all four chemical recovery furnace explosions inspected by the writer during the course of this study has been of the same general pattern but the explosion intensity has varied widely. Two of them produced little easily-evident damage in the furnace up to an elevation one floor above the operating level (approx. 25' above the molten smelt level). Here and above the buckstays became bulged on all four sides. Corner bolts above this level were broken in the case of powerful explosions. In three out of four cases, the corners of the furnace above the operating floor generally split open vertically as designed to meet severe pressure surges. The economizer casing usually was opened. In two of the four explosions substantial (1"-4") deflections were noted in heavy I beams under localized areas of the furnace bottom. Beams were not measured after the first two explosions.

An unusually severe series of multiple explosions occurred over a four minute period in one furnace. The smelt was cleaned thoroughly from the surface of floor tubes in the entire bottom. Two highly localized dish-shaped depressions about a yard in diameter were found in the floor tubes. One, 4 1/2" deep, was near the left rear corner. The other, also 4 1/2" deep, was near the middle of the furnace front close to the center smelt spout. The corner depression matched an approx. 5" localized outward displacement of adjacent vertical water wall tubes extending upward about 4'. The left rear vertical corner (only) of the furnace was ripped open over a 6' vertical distance starting 3' above smelt

level. The 14" wide flange I beams beneath the furnace floor had been deflected 2 1/2 to 4". The furnace roof was opened and minor casing damage to the economizer was incurred. On hydrostatic testing the furnace, a number of leaks were found where wall tubes had been torn loose from welds to channels directly above the corner floor depression. Correspondingly, the depression near the center of the furnace floor matched the location where the ripped smelt spout "can" is believed to have placed water in the molten smelt.

Two consultant explosion specialists examined the damage in this furnace and agreed that the energy density required to create the depressions was far above that which would have been produced by a combustible gas mixture. (4)

(c) Theory on distribution of furnace damage

It is believed that the damage in three furnace explosions and major damage in the fourth was due to a physical smelt-water explosion mechanism. These explosions liberated high density PV energy (in the shock wave range) in a limited area of the furnace bottom where water contacted molten smelt. The decaying explosion pressure wave then spread through the remainder of the furnace structure. The general pattern of damage on furnace structures which at first glance might suggest gas explosions high in the furnace, may instead be the result of the distribution of furnace containment strength and the effects of either a shock wave alone or a shock wave combined with a rapid pressure rise similar in characteristics to a combustible explosion.

In a significant number of chemical recovery furnace explosions, we believe that the distribution of damage observed could not have been caused by a rapid increase in pressure of the total furnace atmosphere in such a large enclosure. In these cases, the distribution of damage can best be accounted for on the basis that it was caused by a shock wave with or without a deflagration wave.

From a study of the available literature, the large scale liberation of flammable gas by chemical reaction of molten smelt and water (if such occurred in a furnace) and its subsequent ignition could not have caused such a shock wave. This follows from the fact that ignition of a limited amount of flammable gas in a furnace would not result in a detonation but rather in a deflagration type of explosion which would not produce a shock wave. A deflagration wave, which can produce a maximum of about 150 psi pressure increase, travels at subsonic speed. Hot gaseous products from the explosive combustion of a flammable gas mixture expand and create a pressure increase through the whole volume of the container. This would hence distribute pressure rather evenly to nearby walls of the furnace.

The postulation that damage was created by a shock wave from the explosive production of steam in chemical recovery furnaces is supported by several observations. These include the following:

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1) Localized depressions in the floor tubes which could not have been created by combustible gas explosions.
2) Since no visible flames were observed to issue from furnace openings in the four recent explosions, a combustible gas explosion is not indicated. Some explosions occurred while there was an actively burning bed in the furnace.
3) The significant deflections of heavy I beams beneath the furnace could not be caused by explosion of combustible gas mixtures. The development of pressure from a deflagration explosion would cause opening of the furnace corners which would relieve the pressure before significant floor beam deflection could occur.
4) From the accounts read, the nature of and damage from plant explosions caused by introducing molten steel, aluminum, and cobalt, as well as molten non-metals like bauxite (Al_2O_3) and sodium chloride into water is strikingly similar to that from smelt-water explosions. None of these former explosions could be attributed to the formation and subsequent oxidation of a flammable gas.

Shock waves, like sound, have directional effects. They can be reflected from surfaces and when wave fronts coincide after reflection, a more powerful force may be applied to a localized area. Shock waves of numerically small pressure magnitude per square inch can create significant damage, as illustrated by data of the following table (5).

Over-pressure* in Shock Wave, PSI	Damage
0.5 to 1.0	Shatters glass windows.
1.0 to 2.0	Shatters corrugated asbestos siding. Corrugated steel or aluminum paneling fails and buckles.
2.0 to 3.0	Concrete wall panels, 8 or 12 inches thick (not reinforced) shatter.
2.5	Moderate damage to light steel frame industrial buildings.
4.0	Moderate damage to medium steel frame industrial buildings and to wall bearing, brick buildings.
5.5	Moderate damage to steel frame office type buildings and to reinforced concrete frame and wall multi-story buildings. Severe damage to wall-bearing brick buildings.

* Pressure above atmospheric

APPENDIX

How can a physical smelt-water explosion in the bottom of a furnace result in damage far above to the casing, corners, refractory, and even in the economizer? Another part of the answer may lie in the distribution of structural strengths in various part of the furnace itself. The bottom and lower welded furnace walls are much stronger than the upper walls and economizer casing. The furnace roof in many designs is also strong. It may be a correct analogy to compare resistance to explosion force between a shot gun with muzzle plugged by mud and a furnace with a smelt explosion in the bottom. In the former case, the muzzle often "banana peels" i.e., splits in several longitudinal sections when fired, while the breech where the shell was exploded remains intact because of its greater tensile strength produced by thicker metal. These opinions should not be assumed to take issue with current furnace design, since it would be technically infeasible to design an explosion damage-proof furnace.

The fact that all explosions to date have been described as "muffled" or "rumbling" probably reflects the sound-deadening effect of the heavier - armored bottom location in which they are believed to occur. (Lab explosions give a short "crack" which implies high velocity. Transducer pressure traces of the shock waves reinforce this view.) The proposed hearth area location of these explosions may provide an explanation also for the extremely low injury rate of personnel who usually work at the smelt spout or operating floor elevations of the recovery furnace.

No chemical recovery furnace explosion to date has been observed by those nearby to expel flames from the furnace openings, although this question is always asked. The operators usually refer only to blinding clouds of steam and finely divided black ash driven from the smelt spouts, liquor gun openings, and fissures in the casing created by the explosion.

For the reasons outlined in this section, it is believed that all four explosion sites recently inspected by the writer involved contact of water or some aqueous solution (other than strong black liquor) with molten smelt. Such explosions are believed to have been physical smelt water explosions which generated shock waves.

REFERENCES

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TYPICAL TIME - PRESSURE TRACE OF A SMELT - WATER EXPLOSION

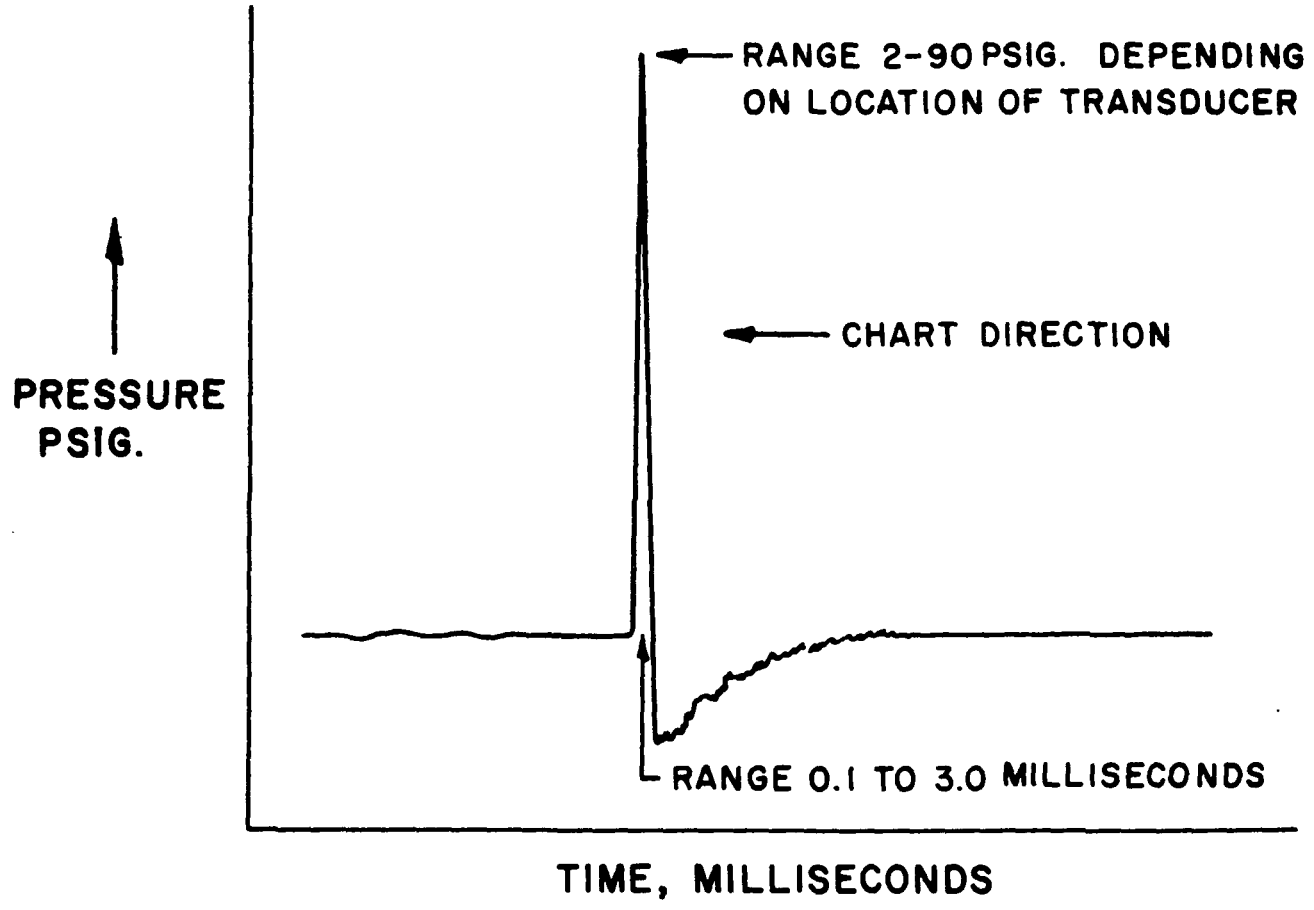
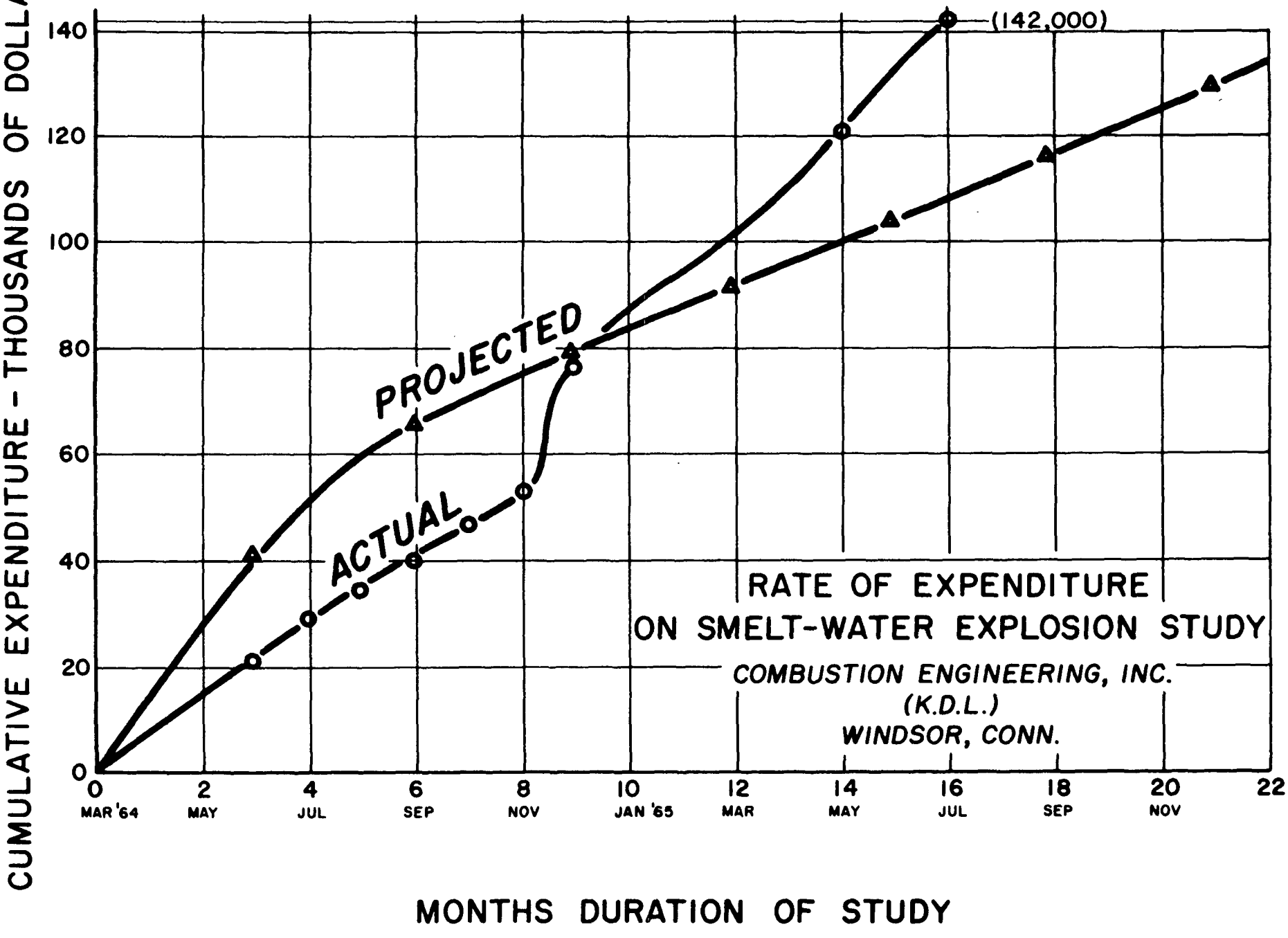


FIGURE NO. 2


CUMULATIVE EXPENDITURE - THOUSANDS OF DOLLARS
140
120
100
80
60
40
20
0
(142,000)
PROJECTED
ACTUAL
RATE OF EXPENDITURE
ON SMELT-WATER EXPLOSION STUDY
COMBUSTION ENGINEERING, INC.
(K.D.L.)
WINDSOR, CONN.
0 MAR '64
2 MAY
4 JUL
6 SEP
8 NOV
10 JAN '65
12 MAR
14 MAY
16 JUL
18 SEP
20 NOV
22
MONTHS DURATION OF STUDY